AMERICAN
DYESTUFF REPORTER

VOLUME XXIII APRIL 23, 1934 NUMBER 9

Recent Developments in the Chemistry of Silk and of Silk Processing--I

By WALTER M. SCOTT, Ph.D.
Gustavus J. Esselen, Inc., Boston, Mass.

Chapter I
THE CHEMISTRY OF RAW SILK

SILK is a product of the silkworm. In spinning its cocoon, the silkworm ejects the contents of its two silk glands through minute spinnerettes, one on each side of its head, to form two threads which are cemented together with a layer of sericin (silk gum) similar in its elementary chemical composition but differing distinctly in physical properties and amino acid content from the central filaments of fibroin (boiled-off silk).

It is the purpose of this article to review the progress which has been made during the last few years in adding to our knowledge of the fundamental chemistry of raw silk, and to summarize from a chemical point of view the improvement which have been made in the processes which transform raw silk into finished fabric.

In 1932 a "Survey of Progress in Textile Research" was compiled by the U. S. Institute for Textile Research. This survey included a chapter on Silk Fiber Research and a chapter on the Technology of Silk Manufacture. These two chapters form an excellent foundation upon which to build the story of subsequent developments in the field of silk chemical research.

For the purpose of the present paper it is proposed to divide the subject into the following chapters:—

I. The Chemistry of Raw Silk.
II. The Soaking of Silk.
III. The Degumming of Silk.
IV. The Weighting of Silk.
V. The Dyeing and Finishing of Silk.

Silk Cocoons and the Silkworm

Very little attention has been paid to the fundamental chemistry involved in the initial stages of silk formation, although naturally the life cycle of the silkworm has been extensively studied from the biological point of view. However, it has been determined that the growth curves of dry matter and of water in the silk gland can be represented by definite equations. The water content of the silk gland of a fully grown larva is about 76%.

On the other hand, it is not advisable to maintain too high a humidity in the room where the silkworms are spinning their cocoons. Lower yields of poorer quality silk are obtained if the moisture of the air in the spinning room exceeds 50 to 75%.

Some very interesting studies have been reported from Italy on the action of ultra-short electromagnetic waves on the development of the silkworms. It was found possible to produce a noticeable acceleration in the life cycle of the silkworm and an increase in the weight of the cocoons by irradiating the silkworm eggs before hatching, or the larvae after hatching, for 30 to 60 minutes daily with ultra - short electromagnetic waves. With a treatment of this sort, the cocoon production began 2 to 3 days earlier and the cocoons were 16 to 24% heavier than normal.

The composition of Hungarian silkworms and their cocoons formed the subject of an analysis published in 1932. The larvae contained 15.48% water, 53.12% raw proteins, 20.09% raw fat and 2.45% mineral matter. The water content of the raw cocoons was 65 to 69%. The raw silk contained an average of 23.2% sericin and 0.9% to 1.5% ash.

The Chemistry of Silk Reeling

A majority of the recent studies on these subjects have been carried out in Japan. This is quite natural when it is considered that Japan produces more raw silk than all the other countries of the world combined. In connection with the reelings of silk, the Japanese have originated the term "Kaijo." The "Kaijo" of cocoons is the weight of raw silk reeled per hour under the same conditions.

The aqueous solutions of cocoon layers of good "Kaijo" have a higher pH than those of poor "Kaijo." It has also been found that the isoelectric points of the aqueous solutions in which reeling is the easiest, lie between pH 4.25 and pH 4.4. As an aqueous solution of the cocoon layer

becomes older, the specific conductivity decreases, the pH and the relative viscosity increase, and there is an increase in the aggregation of the protein molecules, which results in a slight gelatinization. By color reactions, it was shown that an aqueous solution of the cocoon layer which was boiled 30 minutes, probably contained a flavone-like compound, glycocoll, ammonium oxalate, ammonium carbonate, and a very minute quantity of aspartic acid.

A recent American patent claims that a preliminary alkaline treatment is beneficial in promoting the reeling of the silk cocoons. The cocoons are first treated in a dilute solution of a basic ammonium compound, of a concentration below 0.5%, until the solution has penetrated all the cocoon layers. Then they are immersed for at least one minute at room temperature in a 2° Bé. solution of caustic soda, after which they are reeled off in water at room temperature.

The Chemistry of Sericin

The study of the aqueous solutions from which the silk cocoons are reeled, is naturally very closely interwoven with the chemistry of the silk gum (or sericin) which is dispersed in these solutions. Before discussing the recent discoveries in this field it seems advisable to review briefly the extent of our earlier knowledge of this material.

For many years the silk industry has considered sericin somewhat in the light of a necessary evil, which must be removed in a boiling soap solution with the least possible injury to the valuable fibroin. Fortunately the trouble and expense of removing this outer layer of gum was at least partially compensated for by its ability to form stable emulsions in an acid solution. These emulsions provided a very satisfactory medium for the dyeing of the silk.

Although on the whole very reliable, the sericin-soap solution (known as boil-off liquor) would at times break in the acidified dye bath and deposit a quantity of free fat on the silk which was being dyed. The reason for this peculiar behavior was not clearly understood until about 10 years ago, when studies were carried on in the laboratory of Cheney Brothers under the supervision of the author, which demonstrated that the emulsifying power of sericin was practically nullified at a pH of about 4. This was assumed to be the isoelectric point of sericin.

Most of the trouble with broken gum suds emulsions was experienced when acetic acid was used as the acidifying agent in the dye bath. Obviously the breaking of the emulsion was due to the fact that the dye liquor acquired a pH in the neighborhood of the isoelectric point of sericin, at which point it was no longer able to support the emulsion.

Having acquired an understanding of the reasons for this phenomenon, it was a comparatively simple matter to adjust the pH of the dye bath so that it would not approach the danger zone around pH 4. In this manner the trouble with broken gum suds could be almost completely eliminated. Conversely, if it is desired to obtain a recovery of the soap from the degumming bath, this is easily accomplished by bringing the pH of the bath to about 4.1, whereupon the emulsion breaks and the fatty acids rise to the surface with some of the sericin. The pure fatty acids can quite readily be separated from this mixture.

Sericin A and Sericin B

In 1925, Shelton and Johnson demonstrated clearly that silk gum was composed of at least two chemical compounds which they named Sericin A and Sericin B. In 1932 Mosher reviewed the properties of sericin, and brought out the fact that the bulk of the sericin is usually in the form of the "B" modification. The proportion of B varied from a maximum of 86% in Japan silk to a minimum of 44% in Canton silk. The separation of the two types of sericin is made possible because the B type is quantitatively precipitated from solution at its isoelectric point, while the A type remains in solution at this point.

Sericin B is hydrolized into Sericin A in aqueous solutions at high temperatures. The conversion is accelerated in the presence of acids or alkalies. The B type is an excellent dispersing and emulsifying agent, except at its isoelectric point, while the A type is almost devoid of such properties.

Recently the Japanese investigators, Hideo Kaneko and his co-workers, have published a number of papers on the properties of Sericins A and B. The author has not had an opportunity to check their experimental data, or to determine in every case whether their designations of A and B refer to the same types as originally described by Shelton. Nevertheless, a brief summary of their conclusions might be of interest at this point.

(1) Sericin A is more viscous than B and swells more in distilled water. The swelling in water increases with the temperature, especially over 50° C. The swelling is at a minimum near the isoelectric point.

(2) Sericin B is more soluble than A in distinctly acid or alkaline solutions. Both are soluble in the sodium salts of fatty acids. The solubility of A increases while the solubility of B decreases with the number of carbon atoms in the fatty acids.

(3) Sericin as a whole is more soluble in the sodium salts of organic acids than in the sodium salts of inorganic acids i. e., the solubility increases in the following order:—nitrate, chloride, bitartrate, acetate, and citrate. The solubility of sericin in nitrates and chlorides increases with the valence of the metal e.g. the solubility in the

nitrates increases in the following order:—sodium, calcium, aluminum, and zirconium.

(4) Sericin A is coagulated by a solution of ammonium sulfate and can be filtered off from B which remains in solution. Sericin A is also coagulated by the electrodialysis of a sericin solution while B remains in solution. Sericin as a whole is readily coagulated by the nitrates of heavy metals; such as lanthanum, thallium and zirconium. It is also coagulated by such organic solvents as alcohol, acetone, benzol, aniline, chloroform and carbon tetrachloride. A is coagulated in fibrous form and appears to have a micelle structure, while B is amorphous.

(5) After freezing the solution, Sericin A can not be returned to the colloidal state, while B is reversible. Hence A and B can be separated by freezing the dilute solution of sericin. A causes less depression of the freezing point than B.

(6) The isoelectric points of Sericin A and Sericin B are reported to be 4.1 and 4.3 respectively. These results are based on electrophoresis determinations. The isoelectric point is taken to be the point at which there is a minimum movement of the electrically charged particles in the solution.

(7) The apparent specific gravities of Sericin A and Sericin B are 1.358 and 1.309 respectively, when estimated in water at 15° C. In organic solvents also, A has a relatively higher specific gravity than B.

(8) The electrical behavior of sericin resembles that of gelatin. It is also comparable to gelatin in its buffer action. However, the diffusion of organic coloring matters in sericin gel is slower than in gelatine or agar agar.

(9) The gold number of sericin ranges from 0.02 to 0.038. This indicates that sericin as a protective colloid is approximately equal to egg globulin, gelatin and egg albumin. The maximum gold number of sericin is found at its isoelectric point. The gold number of Sericin A is smaller than that of B under the same conditions.

(10) The nitrogen distribution is considerably different in A than in B. Sericin A is especially rich in the amino acid, arginine. It contains 2.62% of tyrosine and 6.18% of glycine, while B contains 5.53% of tyrosine and 4.89% of glycine.

The total nitrogen content of pure sericin is given by an Italian investigator as ranging from 16.48 to 16.66%.

The Coloring Matter of Silk

The coloring matter in yellow cocoons consists largely of xanthophyll. Crude xanthophyll extracted from cocoons may be purified by crystallization from a mixture of methanol and petroleum ether. The purified xanthophyll melts at 193° C. The decolorization of the yellow cocoons in the air is shown to be caused by oxidation of the xanthophyll. Carotene, lutein and violaxanthin have also been identified in the extract from yellow cocoons.

The Chemistry of Fibroin

Fibroin, as well as sericin, is a protein and a member of the group of compounds known as polypeptides. These compounds consist of more or less closely knit aggregates of amino acids. It is possible to obtain some insight into the molecular structure of fibroin by studying the products of its hydrolysis. In 1922, Abderhalden published the following list of amino acids which he obtained by hydrolysis of the fibroin obtained from the common silkworm Bombyxmori:—

40.5% glycine, 25.0% alanine, 11.0% tyrosine, 2.5% leucine, 1.8% serine, 1.5% arginine, 1.5% phenylalanine 1.0% proline, 0.85% lysine, and 0.75% histidine. These percentages total to about 85%, which leaves about 15% of the fibroin unaccounted for.

In 1932 Abderhalden reported that, as a result of a more careful hydrolysis of fibroin from the same source, he was able to isolate and identify the following amino acids in addition to those mentioned above: norvaline, valine, chitosamine, aspartic acid, glutaminic acid and glucuronic acid. Also, by treating the fibroin for 40 hours at 37° C. in a normal solution of sodium hydroxide, he was able to obtain a partial hydrolysis and to isolate the pentapeptide, glycylserylprolyltyrosylproline as well as the tetrapeptide, serylprolyltyrosylproline.

By using the methods of hydrolysis developed by Abderhalden, three Chinese chemists recently determined that Chekiang silk contained 35% glycine ester hydrochloride, 16.5% alanine, and 10.5% tyrosine. The tyrosine content was practically the same as in Japanese and Italian silks, but the percentages of glycine and alanine were somewhat lower.

Studies on the chemical structure of fibroin have been made from a somewhat different angle of approach. It has been found that fibroin can be benzoylated by heating with benzoyl chloride either in a pyridine or a water solution, and the percentage of benzoyl which is taken up in this reaction can be determined. Fibroin will also react with resorcinol when fused with this product for about 13 hours in an atmosphere of nitrogen. The reaction product may be separated into fractions soluble in resorcinol-water, ethyl alcohol, and meta cresol respectively, and an insoluble residue. The more soluble fractions have a lower nitrogen content and contain resorcinol in chemical combination.

The Isoelectric Point of Fibroin

Von Weimarn, in 1913, paved the way for studies on the isoelectric point of fibroin, when he discovered that stable solutions of fibroin could be obtained by means of concentrated aqueous solutions of certain salts. Prior to this time, the dissolving of fibroin in acid or alkaline solutions was always accompanied by hydrolysis and consequence decomposition. The solubility of fibroin in various salt solutions will be discussed in a later section. For

the moment, we will deal with the determinations of pH in the fibroin solutions thus prepared. Much of the recent work on this subject has been contributed by Dr. Milton Harris, Research Associate of the American Association of Textile Chemists and Colorists.

There are several methods by which the isoelectric point of a material in solution may be determined. In connection with solutions of fibroin, the effect of pH upon the following properties has been studied: (1) solubility, (2) viscosity, (3) the migration of electrically charged particles (called cataphoresis or electrophoresis), and (4) the combination with positive and negative ions. The first three methods serve to establish the isoelectric point quite definitely, while the fourth merely delineates an isoelectric region.

The isoelectric point of the fibroin from the common silkworm, Bombyxmori has been placed at 2.1 by the method of minimum solubility, 2.3 by the method of minimum viscosity, and 2.5 by the method of minimum migration (or mobility) of particles in an electrical field. Fibroin will combine with the negative ferrocyanide ion up to a pH of about 4.0, and with the positive nickel ion down to a pH of about 1.8.

The isoelectric points of certain wild silks have been recently determined by the Japanese investigator, Bito. He reports the isoelectric point of Tussah at pH 2.79, and Kuriwata at 2.85. Solutions of silk from the wild silkworms Antheraea pernyi and Dictyoploca japonica have isoelectric points of 2.6 and 2.8 to 2.92 respectively.

Practical Applications of the Chemistry of Fibroin

Studies on the hydrolysis of fibroin in solutions of varying hydrogen ion concentrations, show the necessity of keeping within certain pH limits during the processing of silk. The decomposition of fibroin is much more rapid in alkaline than in acid solutions. For example, after a 10 hour treatment with a normal solution of caustic soda, approximately 45% of the original fibroin is converted into amino acids. After a similar treatment in a three normal solution of hydrochloric acid, only about 10 or 15% of the fibroin is converted.

It is evident that there is not much need to worry about the loss in strength of silk while processing in acid solutions, because the concentrations of acid required in the usual dyeing and finishing processes, are not sufficient to materially affect the fibroin. On the other hand, in the removal of the silk gum by boiling in a soap solution, the alkalinity of the bath is close to the pH at which the fibroin is quite seriously affected. It is always advisable to use soaps sufficiently neutral so that the pH of the solution is not above 10.5. This matter will be discussed further in a later section on degumming.

Curiously enough, although fibroin is particularly sensitive to the action of alkaline solutions, it is less sensitive to deterioration upon exposure to light when finished in an alkaline solution than when finished in an acid solution. Harris and Jessup have reported that silk finished in a bath whose pH is about 10, loses less tensile strength after exposure to light for a period of time, than silk finished at any other pH, either acid or alkaline. When finished at a pH below 3 or above 11, the breaking strength of silk decreases very rapidly under the action of light.

The Solubility of Fibroin

It has been stated previously in this article that fibroin will swell and can be dissolved without decomposition in concentrated aqueous solutions of certain salts. Harris and Johnson have reported studies with the chlorides, bromides, iodides, nitrates, thiocyanates and chlorates of calcium, strontium, barium and lithium. Both the anions and the cations are listed in the order of their increasing solvency action on fibroin. Other neutral salts which have more or less swelling action on fibroin are sodium and nickel nitrates; also sodium, cobalt, magnesium zinc, aluminum and iron chlorides. In actual practice a 70% solution of calcium thiocyanate has been found to be a very satisfactory solvent for silk.

Fibroin, as well as cellulose, is soluble in an alkaline solution of copper oxide, where the alkalinity is usually furnished by ammonium hydroxide or an amine. In Schweitzer's solution, the fibroin is dissolved so rapidly that 90% is dissolved within one-half hour, and the solution is practically complete within 4 hours. In mixtures of copper hydroxide with glycerol, fibroin behaves somewhat differently. The fibers first break into short pieces which then dissociate into fibrils. From the solution of fibroin in copper oxide-ethylenediamine, there have been isolated two complex fibroin- copper-amine compounds with the approximate ratios of 1:1:1 and 1:2:2 respectively.

Within the last few years, the patent literature bears evidence that serious attempts are being made to commercialize the solution of fibroin and its coagulation in the form of fiber. It is of interest to mention at this point some of the more promising procedures which have been recently protected by patents.

(1) Cuprammonium Solutions:—Use not more than 4 mols. of ammonia (NH_3) to one mol. of copper (Cu), and not more than 4 parts of copper (calculated as $Cu(OH)_2$) to 10 parts of air dry fibroin. The solution should be prepared and kept at temperatures below 0° C. An addition compound of copper and fibroin is precipitated from this solution as a violet-black paste by the addition of alcohol, acetone, a solution of ammonium sulfate, or acetic acid. The paste can be dissolved in water to give stable solutions for spinning. The neutral or weakly alkaline fibroin solutions are forced through nozzles into a precipitating bath of an acidified concentrated salt solution. Salts of sulfuric acid or acetic acid are recommended for this purpose.

(2) Other Alkaline Hydroxide Solutions:—Ammoniacal solutions of zinc or cadmium hydroxides in combination with copper or nickel hydroxides, are mentioned as solvents for fibroin.

(3) Thiocyanates:—Fibroin will dissolve in concentrated solutions of sodium or calcium thiocyanate. Solutions of fibroin in sodium thiocyanate are more homogeneous and less viscose if an amide (such as acetamid or urea) is present. Mixtures of thiocyanates with alkal or alkaline earth halides are also recommended.

(4) Other salts:—Mention has been made of lithium bromide, sodium iodide, calcium chloride, and magnesium nitrate. Silk is dissolved in concentrated solutions of these salts at temperatures not exceeding 80° C, or kneaded with the hydrated salts and then dissolved in water.

(5) Acids:—Fibroin may be dissolved without decomposition in syrupy orthophosphoric acid or sulfuric acid of 25 to 75% concentration, if the temperature is kept below 10° C. It is subsequently coagulated at the same low temperatures in water or in alcohol. Fibroin will also form a concentrated solution in formic acid in the presence of small proportions of calcium chloride, zinc chloride, thiocyanates, or phosphoric acid.

(6) Anhydrous Ammonia:—Silk will dissolve in liquid ammonia at about —77° C. The solution of the fibroin is aided by the presence of small amounts of salts—such as potassium, calcium or magnesium nitrates, or potassium thiocyanate—although these salts are not absolutely essential. The ammonia is driven off by raising the temperature and the residue may then be dissolved in water.

Additional Properties of Fibroin

During the past few years several workers have devoted their attention to the physical properties of fibroin, and particularly to the effect of moisture on its tensile strength. It is reported that wetting with pure water decreases the tensile strength of silk but increases its elongation. Changes in the relative humidity of the atmosphere, have a similar, though less pronounced effect. Acidic solutions increase its tensile strength but decrease its elongation, while alkaline solutions cause a decrease in both factors. The values of the breaking load, and the extension at the break, of a silk fiber, depend upon the rate at which the fiber is extended.

The lateral swelling of silk fibroin has been determined in solutions whose pH varies from one to nine, and in air at relative humidities from zero to one hundred. The maximum swelling in air of 100% humidity is 18.7% for Japanese silk and 16.3% for Italian silk.

The moisture regains of Japanese, Chinese, and Italian silks are approximately the same at any definite relative humidity of the atmosphere while the regain of Tussah silk is always higher under similar conditions. The following table shows the comparative regains of these silks at varying humidities.

Moisture Regain Table

Relative Humidity	%	92.8	79.7	53.7	40	21.5
Italian Silk Regain	%	16.9	12.2	9.3		5.4
Chinese Silk Regain	%	16.9	12.2	9.3	7.5	5.3
Japanese Silk Regain	%	17.0	12.3	9.3	7.6	5.3
Tussah Silk Regain	%	17.9	12.8	10.0	8.0	5.9

Internal Structure of Fibroin and Sericin

X-ray investigations of several different types of fibroin indicate that a protein of definite crystalline structure is common to all of them. Clark states that the crystal system in fibroin is monoclinic. He assumes that the chains of amino-acid residues are bound together in peptide linkage to form long spiral macromolecules, with 4 alanyl glycyl residues per unit cell.

Recently a Japanese physicist reported that sericin also contains regularly arranged crystalline micelles. He gave the positions of index ellipses both in sericin and in fibroin.

Fibroin is entirely exposed by boiling at 100° C. for 10 hours, or at 150° C. for 3 hours. The intermicellar fissures of fibroin are markedly changed at 150° C, with the results that they are dyed violet by Oxamine Blue R. However, the lattice structure of fibroin remains almost unchanged if it is dissolved in a neutral salt solution, or a cuprammonium solution, and then coagulated into the fiber form again.

(To be continued)

TEXTILE FOUNDATION NEWS

Possibility of United States Flax Production and Utilization Being Studied

During recent months there has been a revival of interest in the subject of flax production, preparation and utilization in the United States. This country has no important linen industry, as such, although it is a very large user of flax and flax products, ranging from coarse twines to the finest damasks. Flax fiber is utilized for many other purposes, some of the more important being the manufacture of paper, apparel, towels, and handkerchief fabrics.

Because of this interest in flax, the Textile Foundation called a meeting in Washington, D. C., of leading chemists, paper and textile manufacturers, flax growers, technicians, government officials and others, who had had experience in different phases of flax with a view to obtaining their cooperation and advice.

As a result of the facts brought out at this meeting the Foundation has decided to launch a series of investigations and experiments ranging through the field of production, machine and chemical preparation, utilization in the manufacture of paper, and the production of linen fabrics on cotton mill machinery. If the production of flax in the United States proves successful, the farmer will have an added crop. The American grown flax will not interfere with cotton but may supplant some of the raw flax imported into the United States for manufacture into certain products.

H. H. Willis, in addition to his duties as Dean of the Textile School of Clemson College, Clemson College,

S. C., will devote part of his time to correlating the different activities and seeing that they move forward with reasonable speed.

A limited amount of pedigreed flax seed has been obtained and arrangements made for its planting in different localities of the following states: Virginia, West Virginia, North Carolina, South Carolina, and Tennessee. Flax production by private enterprise in Georgia and in South Carolina will be included in this study.

The Textile Foundation, Washington, D. C., was organized four years ago for scientific and economic research for the benefit and development of the textile industry and its allied branches, including that of production of raw materials. The present directors are Franklin W. Hobbs, President, Arlington Mills, Boston, Mass., chairman; Stuart W. Cramer, President, Cramerton Mills, Cramerton, North Carolina, Treasurer; Henry A. Wallace, Secretary of Agriculture; Daniel C. Roper, Secretary of Commerce and Frank D. Cheney, Cheney Brothers, New York, N. Y. Edward T. Pickard, Chief, Textile Division, Department of Commerce, is Secretary of the Foundation.

To Discuss Warp Sizing of Cotton and Rayon

The sizing of cotton and rayon warps will be discussed at a conference to be held by U. S. Institute for Texitle Research, Inc., at the Hotel Commodore, New York City, Friday, May 11, starting at 10 A. M. This is the second of a series of open conferences designed by U. S. Institute to survey important textile problems suggested for scientific research, and, through discussion by authorities on the subject, to determine what the problem is and what needs to be done to solve it.

The first of these conferences was held at the Hotel Commodore March 24, when the subject of Fabric Wear Resistance and Wear Testing was discussed by some 70 authorities, the result of which is a study of correlation of service wear and machine testing that is being conducted at the U. S. Bureau of Standards under the direction of Dr. H. F. Schiefer.

The sizing of warps as well as the sizing of finished goods is mainly a problem of colloid chemistry, but thus far little has been done to apply in textile sizing the voluminous new knowledge of that branch of chemistry. This is the phase of the subject on which the conference will endeavor to concentrate, and it is hoped that the survey of warp sizing may lead to the broader subject of finished goods sizing.

Some idea of the lack of standardized practice in warp sizing may be gained from the following statement of the chairman of a group meeting on the subject held by the National Association of Cotton Manufacturers: "I will gamble that there are no two dressers in this room that have the same size formula, that use the same materials, or do the job the same way. If the Textile Foundation wants a real problem to solve, here is one."

The conference is open to all who are interested in the subject, and program and reservation for luncheon may be obtained by addressing C. H. Clark, Secretary, U. S. Institute for Textile Research, Inc., 65 Franklin St., Boston, Mass.

NEW PATENTS

(*Abstracted by S.O.C.M.A.*)

Vat Dyestuffs of the Dibenzopyrene-Quinone Series. (More specifically, halogenated 3.4.8.9-dibenzopyrene-5.10-quinones; dye cotton yellow shades.) Max Albert Kunz, Mannheim, and Karl Koeberle, Ludwigshafen-on-the-Rhine, Ger., assignors to General Aniline Works, Inc., N. Y., N. Y., No. 1,952,677, 3/27/34.

Condensation Products of the Anthraquinone Series. (For use as dyestuff intermediates and as dyestuffs, the latter dyeing very fast shades having a great variety of colors according to the reaction components used; for example, comprises heating a 1-amino-anthraquinone-2-carboxylic ester in an inert organic solvent with a dibromo-3.4.8.9-dibenzopyrene-5.10-quinone.) Max Albert Kunz, Mannheim, and Karl Koeberle, Ludwigshafen-on-the-on-the-Rhine, Ger., assignors to General Aniline Wks., Inc., N. Y., N. Y., No. 1,952,678, 3/27/34.

IF you find time at the Knitting Arts Exhibition in Philadelphia this week we shall be very glad to see you at the

HOWES PUBLISHING CO.

BOOTHS NUMBERS

131 — 132 — 159 — 160

A. P. HOWES
President

M. D. REESER
Adv. Manager

PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

APRIL 23, 1934

Officers of National Association

ROBERT E. ROSE, *President*
E. I Du Pont de Nemours & Co., Wilmington, Del.

A. R. THOMPSON, Jr.—ALEX MORRISON, *Vice-Presidents*

WILLIAM R. MOORHOUSE, *Treasurer*
National Aniline & Chemical Co., Boston, Mass.

HAROLD C. CHAPIN, *Secretary*
Lowell Textile Institute, Lowell, Mass.

Councillors

JOSEPH F. X. HAROLD
DONALD H. POWERS
CARL Z. DRAVES
WILLIAM D. APPEL
HUGH CHRISTISON
WALTER M. SCOTT

President Emeritus and Chairman of the Research Committee
LOUIS A. OLNEY
Lowell Textile Institute, Lowell, Mass.

Council Representatives: Northern New England—Roland E. Derby, New York—Hans Meyer, Philadelphia—Harold B. Dohner, Midwest—Carl E. Bick, South Central—G. H. Dubois.

Local Sections and Their Officers

Northern New England Section
Leverett N. Putnam, Chairman, Worsted Division, Pacific Mills, Lawrence, Mass.
Clarence L. Nutting, Secretary, Arlington Mills, Lawrence, Mass.

Rhode Island Section
Heyward F. Lawton, Chairman, Borden & Remington Co., Providence, R. I.
C. Brian Wainwright, Secretary, Apponaug Co., Apponaug, R. I.

New York Section
Henry F. Herrmann, Chairman, General Dyestuff Corp., 230 Fifth Ave., New York City.
Thomas R. Harris, Secretary, Herrick & Voigt, 21 West St., New York City

Philadelphia Section
William A. Stringfellow, Chairman, Ankokas Mills, Mount Holly, N. J.
Charles A. Seibert, Secretary, 39 Chestnut St., Salem, N. J.

Piedmont Section
George P. Feindel, Union Bleachery, Greenville, S. C.
John C. Robertson, E. I. du Pont de Nemours & Co., 5 Pettigru St., Greenville, S. C.

South Central Section
Harold Schroeder, Chairman, Dixie Mercerizing Co., Chattanooga, Tenn.
Harvie Bruce Kimbell, Secretary, Dixie Mercerizing Co., Chattanooga, Tenn.

Midwest Section
Eric F. Hempel, Chairman, National Knitting Co., 2165 South First Street, Milwaukee, Wis.
Elmer F. Smith, Secretary, American Aniline Products, Inc., 820 S. Clinton St., Chicago, Ill.

South-Eastern Section
Charles B. Ordway, Chairman, Alabama Polytechnic Institute, Auburn, Ala.
C. A. Jones, Secretary, Georgia School of Technology, Atlanta, Ga.

Lowell Textile Institute Student Section
Raymond L. Matthews, Chairman; Charles L. Daley, Secretary.

North Carolina State College Student Section
H. S. Blinens, Chairman; D. B. Hardin, Secretary.

Members should notify the **Secretary** immediately of all address changes

The Carbonization of Wool

EXTENDING over a period of nearly two years the Research Committee of the American Association of Textile Chemists and Colorists, has been making a study of the chemical and physical principles which are involved in the process of wool carbonization. The Sub-Committee on Carbonization* has acted in an advisory capacity, and the research work has been conducted by Milton Harris working at the Bureau of Standards, and Bertil A. Ryberg at the Lowell Textile Institute. We are publishing at this time the results of this work, as far as completed, in three separate papers.

The first, by Milton Harris entitled, *The Carbonization Process—A Study of the System Wool-Sulfuric Acid-Water*, which deals chiefly with chemical and physical principles involved in the soaking of wool with sulfuric acid of various dilutions and the subsequent drying of the wool and final baking with the residual sulfuric acid, in contact with the fiber.

The second, by Bertil A. Ryberg entitled, *A Study of the Carbonization Process and Its Effect on the Dyeing Properties of Wool;* which deals more specifically with the modifications in dye absorbing properties of wool brought about by the carbonizing process, and explanations of causes of the irregularities which so frequently cause trouble in the dyeing of carbonized wool.

The third, by Roland E. Derby, chairman of the Sub-Committee, gives an Interpretative Resume for the benefit of textile manufacturers who may not be able to follow all of the highly technical and chemical nomenclature involved in the first two papers.

This research work upon the important process of wool carbonization, which we believe is the most complete and thorough study of the subject that has heretofore been undertaken, has been made possible through allocations to our Association by the Textile Foundation, and the Research Committee wishes to express to the Directors of the Foundation their appreciation of the valuable service thus rendered to the Association and, we believe, to the Textile Industry as well.

The Committee also wishes to express its appreciation for the valuable assistance rendered by the Bureau of Standards and the Lowell Textile Institute in whose laboratories the experimental work was largely conducted.

L. A. OLNEY,
Chairman Research Committee

* Roland E. Derby, Chairman; Harold W. Leitch, Claxton Monro, Alex. Morrison, Louis A. Olney.

Proceedings of the American Association of Textile Chemists and Colorists

The Carbonizing Process[1]

A Study of the System Wool-Sulfuric Acid-Water

By MILTON HARRIS[2]

The purpose of this study was to provide quantitative data on the system wool-sulfuric acid-water under conditions similar to those in the soaking, drying and baking of wool in the carbonization process as a basis for the effective study of mill problems relating to the process.

The amount of sulfuric acid absorbed by wool from 0.1, 1, and 5 per cent solutions at 22° C. and from a 5 per cent solution at 35° C. and the rates of absorption are reported. It was found that the wool treated with acid retains less moisture than similar wool treated only with water when dried in air of relative humidities 6, 30, 65 and 90 per cent, the difference in the amount of water absorbed being greatest for the 30 and 65 per cent relative humidities. When the dried wool is baked there is a critical moisture content for each concentration of acid in the wool above which the breaking strength of the wool decreases and the ammonia nitrogen content increases. The physical and chemical break-down increases with an increase in concentration of acid and with an increase in the temperature of baking. The deterioration takes place in the first few minutes of baking.

When acid treated wool is stored in air of 65 per cent relative humidity or less, there is no decrease in breaking strength, but there is chemical deterioration as evidenced by the ammonia nitrogen content which increases with time of storage. The higher the relative humidity of the atmosphere in which the wool is stored and the greater the concentration of acid in the wool the more rapid is the increase in ammonia nitrogen content.

That the deterioration of wool in baking is promoted by the presence of oxygen, moisture and sulfuric acid is demonstrated in experiments in sealed tubes.

The nature of the system wool-sulfuric acid-water is discussed. Mechanisms by which moisture and acid may be taken up and held by wool are suggested.

I. Introduction

THE object of the carbonizing process is the removal of vegetable matter, which cannot be removed conveniently by mechanical means, from wool. The wool is impregnated with a solution of sulfuric acid[3], extracted to remove the adhering acid liquor, dried at about 160° F., baked at about 250° F., dusted in the raw stock or dry milled in the piece, and finally rinsed or neutralized. The control of the process to avoid damage to the wool must be considered one of its important phases. It is probable that many if not all of the troubles in the subsequent processing of wool that are attributable to faulty carbonization arise from incipient damage to the wool.

A considerable amount of acid is absorbed by wool in the carbonization process. A knowledge of the nature of the wool - acid combination and the effect of the variables concerned is obviously basic to the control of carbonization. It is of importance from the standpoint of subsequent processing of the woolen or worsted pieces, for example, dyeing from acid solutions. The purpose of this research is to supply quantitative data on the system wool-sulfuric acid- water as a basis for the effective study of mill problems relating to the carbonization process.

The variations in the carbonization process as practiced in industry make it difficult to attempt to set up any one laboratory procedure to cover all of the conditions. Moreover, it was evidently desirable to carry out the experiments under conditions that could be strictly controlled in order to obtain reproducible quantitative values. A large excess of acid over wool was used in the soaking bath and soaking was continued until equilibrium was reached, to insure uniform distribution of the acid in the fiber. Similarly, in drying and baking the wool was well exposed to the surrounding atmospheres. The conditions of these experiments may be considered to be "ideal" rather than practical, but it is believed that the results have considerable practical significance.

II. Material and Methods

The material used for the experiments was worsted cloth, plain weave weighing 8 ounces per running yard, mill-processed ready for dyeing. It was purified in the laboratory by successive extractions of 24 hours each with alcohol and ether and, finally, was soaked in water at 60° C. for 30 minutes to remove adsorbed solvents[4]. After air drying, the cloth was cut warpwise into specimens measuring 3½ by 6 inches.

The breaking strength of the cloth was taken as a measure of its physical breakdown in the experiments. A pendulum type testing machine and the strip method were used. Specimens 6 inches long and 1 inch wide, cut warpwise of the cloth, were tested. All specimens were thoroughly conditioned and tested in a room maintained at a relative humidity of 65 per cent and a temperature of 70° F. The average strength of from three to five specimens is reported.

The amount of wool protein in a specimen at any stage of processing was obtained by determining the total nitrogen by the Kjehldahl method. This value multiplied by

[1]The work reported here was made possible by a grant from the Textile Foundation, Incorporated, to the American Association of Textile Chemists and Colorists.

[2]Research Associate for the American Association of Textile Chemists and Colorists at the Bureau of Standards.

[3]Aluminum chloride and hydrochloric acid are sometimes used instead of sulfuric acid. These reagents are not considered in this paper.

[4]R. T. Mease, Adsorption of alcohol by fibrous materials. Ind. and Eng. Chem., Analytical Edition, vol. 5, p. 317 (1933).

the factor 6.33 (obtained by dividing a known weight of the purified wool by its nitrogen content) gave the figure taken for the amount of wool protein.

The chemical breakdown of the fiber in the experiments was followed by analyzing specimens for ammonia nitrogen; that is, that portion of the nitrogen which is liberated when the wool is boiled in a saturated solution of magnesium oxide.

Experiments in which specimens were exposed to air of different relative humidities were carried out by suspending the specimens in desiccators containing suitable saturated salt solutions. The salts used and the relative humidities are indicated in Table 1.

Table 1
Relative Humidities Over Saturated Solutions

	Relative Humidity
Sodium Hydroxide (NaOH)	6[18]
Phosphoric Acid ($H_3PO_4.½\ H_2O$)	9[18]
Sodium Chloride, Potassium Nitrate and Sodium Nitrate (NaCl KNO_3 and $NaNO_3$)	30[19]
Zinc Sulfate ($ZnSo_4.7H_2O$)	90[20]

The moisture content of the wool specimens was determined with the apparatus shown in Figure 1. The specimen is placed in Chamber A. The U-tube B is immersed in liquid air. The apparatus is then evacuated. The moisture from the specimen passes over into the U-tube where it freezes. It is then weighed directly. D is a cotton plug to prevent particles of ice from passing out of the tube. The rate of removal of moisture from wool by this method is slower than oven drying, equilibrium being reached in 24 to 30 hours. However, oven drying at temperatures above 100° C. was found to be unsatisfactory, especially when much acid and water were present. Not only was it difficult to obtain a constant weight, but when the moisture and acid concentrations were high, the wool was degraded.

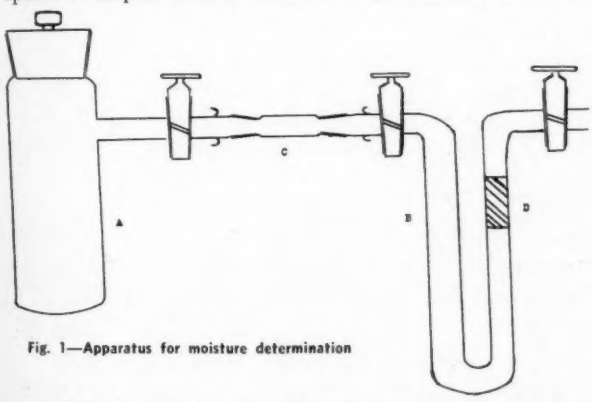

Fig. 1—Apparatus for moisture determination

The amount of sulfuric acid present in an acid treated wool specimen was determined as barium sulfate by the following procedure. A two-gram specimen of the wool was dissolved in 50 ml. of an aqueous 5 per cent solution of potassium hydroxide by warming on a steam bath. The solution was made slightly acid with hydrochloric acid. Twenty ml. of a 10 per cent solution of barium chloride was added. The solution was filtered and the precipitate was washed with water until free from chloride and then ashed in an electric muffle furnace at 700° to 800° C.[5]

III. Experimental

(1) *The Distribution of Sulfuric Acid Between Wool and Water in the Soaking Bath.*

Two-gram specimens of wool were soaked in 50 ml. portions of 0.1, 1 and 5 per cent solutions of sulfuric acid. At intervals of time, the pH value of each solution was determined with the hydrogen electrode. For concentrations of acid greater than 1 per cent, there was little if any variation in pH value because the quantity of acid taken up by the wool was very small compared with the amount present,

The amount of sulfuric acid absorbed by the wool as a function of time was determined. Specimens of the conditioned wool cloth containing 2 grams of wool protein were placed in flasks with 50 ml. portions of sulfuric acid solution and the flasks were kept at a temperature of 22° C. The flasks were shaken frequently. At stated intervals, aliquots were taken from the flasks and titrated with standard sodium hydroxide solution. Only one aliquot was taken from each flask. The decrease in acid present in solution, or absorbed acid, obtained for each time interval is the average of three titrations. The results are shown in Figure 2 in which the milli-equivalents of absorbed acid are plotted as a function of time. The amount of acid absorbed increases with increasing acid concentrations up to 5 per cent.

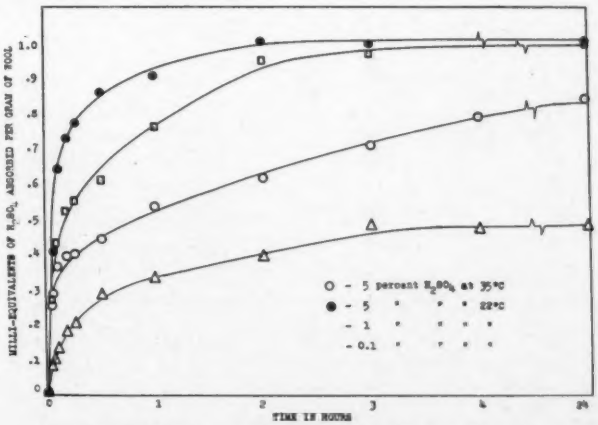

Fig. 2—Rate of absorption of sulfuric acid by wool

[5]Analyses of purified wool and of purified wool plus known amounts of sodium sulfate indicated that this method gives results satisfactory for present purposes. R. T. Mease of the Bureau of Standards is making a study of methods for analysis of wool for total and sulfate sulfur.

[18]Obermiller—Die Einstellung von Luft, Z. phys. Chem., vol. 109, p. 145 (1924).

[19]Bronsted, Kgl. Danske Vidensab. Selskak, Math. fys. Medd., vol. 1, p. 5 (1918).

[20]Sedgewick and Eubank, J. Chem. Soc., vol. 125, p. 2268 (1924).

The curve through the solid circles in Figure 2 shows the rate of absorption of acid by the wool cloth when it was soaked in a 5 per cent solution of sulfuric acid at 35° C. The rate of absorption evidently increases with increase of temperature. However, the amount of acid absorbed at equilibrium is nearly the same as the amount absorbed in a 5 per cent acid solution at 22° C.

(2) *The Wool-Acid-Water System When the Wool is Dried*

Specimens of wool were soaked in a 5 per cent solution of sulfuric acid at 22° C. for 3 hours and centrifuged for 3 minutes. They were then exposed to atmospheres of 9, 30, 65, and 90 per cent relative humidities at 70° F. The samples were analyzed for sulfate, moisture, and wool protein. The values in table 2 are given in grams per gram of wool protein taken at equilibrium and each is the average of three determinations.

Table 2

Moisture and Sulfate Contents of Wool Specimens Treated with 5 Per Cent Sulfuric Acid and Exposed to Atmospheres of Different Relative Humidities at 70° F. Quantities Are per Gram of Wool Protein.

Relative Humidity	Moisture	Sulfate
Percent	Gram	Gram
9	0.0380	0.0813
30	.1118	.0810
65	.1372	.0806
90	.2484	.0810

The moisture contents of wool soaked in 2.5 and 5.0 per cent solutions of sulfuric acid, centrifuged and dried to equilibrium with atmospheres of different relative humidities and the moisture contents of similarly dried untreated wool are recorded in Table 3.

Table 3

Moisture Contents of Acid Treated and Untreated Wool Specimens After Exposure to Atmospheres of Different Relative Humidities.

1	2	3	4
Relative Humidity	H_2O per gram Wool protein	H_2O per gram Wool protein Untreated	Difference (3-2)
Treated with 2.5% H_2SO_4			
Percent	Milli-mols	Milli-mols	
6	1.98	2.47	0.49
30	5.19	6.19	1.00
65	7.37	7.98	0.61
90	9.73	9.99	0.26
Treated with 5% H_2SO_4			
6	1.81	2.53	0.71
30	5.09	6.29	1.20
65	7.41	7.96	0.55
90	10.04	10.22	0.18

The wool treated with sulfuric acid absorbs less moisture than untreated wool. The difference in the amount absorbed varies with the relative humidity, a maximum difference being reached between 6 and 65 per cent relative humidity. This observation will be discussed later.

(3) *The Wool-Acid-Water System When the Dried Wool is Baked*

Specimens of the wool cloth were soaked for 3 hours at 22° C. in 2.5, 5.0, 7.5, and 10 per cent solutions of sulfuric acid and centrifuged. They were exposed to atmospheres of different relative humidities and then baked for different lengths of time. Samples containing 40 per cent or more moisture were obtained by squeezing the excess liquor from the wool. Samples prepared this way contained only a very slightly larger amount of acid. This moisture contents of duplicate specimens which were not baked were determined. The baking was done in a laboratory electric drying oven (inside dimensions 1′ x 1′ x 1′). A beaker of water was kept in the oven in order to maintain high relative humidity.

The breaking strengths and ammonia nitrogen contents of the specimens after baking were determined as already described. The results are given in Table 4.

These data indicate that for each acid concentration there is a critical moisture content above which the breaking strength of the cloth decreases and the ammonia nitrogen content increases when the wool is baked. Thus the critical moisture content of wool soaked in 2.5 per cent sulfuric acid is about 50 per cent, for 5 per cent acid about 40 per cent and for 7.5 per cent about 30 per cent. The increase in ammonia nitrogen serves as a

Table 4

Effects of Acid and Moisture Contents and Time and Temperature of Baking on the Breaking Strength and Ammonia Nitrogen Contents of Wool Specimens.

H_2O in Specimen before baking	Time of baking	Temperature of baking	Breaking strength 1 in. strip	Ammonia nitrogen per gram of specimen after baking*
Percent	Minutes	° F.	pounds	Milligrams
Original	—	—	27	0.20
12	60	250	27	0.54
Wool Soaked in 2.5% Sulfuric Acid (0.058 gm. H_2SO_4 per gram wool protein)				
3	60	250	27	.58
9	60	250	27	.54
12	60	250	27	.64
21	60	250	27	.59
30	60	250	27	.71
50	60	250	26	1.01
65	60	250	23	1.25

Table 4—Continued

H_2O in Specimen before baking	Time of baking	Temperature of baking	Breaking strength 1 in. strip	Ammonia nitrogen per gram of specimen after baking*
Percent	Minutes	° F.	pounds	Milligrams
Wool Soaked in 5% Sulfuric Acid (0.081 gm. H_2SO_4 per gram wool protein)				
3	60	250	27	1.06
9	60	250	26	.96
12	60	250	26	.98
21	60	250	27	.96
30	60	250	27	1.09
40	60	250	25	1.15
50	15	250	23	1.53
50	30	250	22	1.59
50	45	250	23	1.50
50	60	250	23	1.52
64	15	250	20	1.66
64	30	250	19	1.72
64	45	250	19	1.65
64	60	250	20	1.60
50	60	225	27	1.50
50	60	200	25	1.38
50	60	175	25	1.30
50	60	150	25	1.41
Wool Soaked in 7.5% Sulfuric Acid (0.098 gm. H_2SO_4 per gram wool protein)				
3	60	250	27	1.38
9	60	250	26	1.49
12	60	250	27	1.33
21	60	250	24	1.47
30	15	250	14	2.33
30	30	250	16	2.30
30	45	250	15	2.51
30	60	250	14	2.42
50	60	250	9	3.19
Wool Soaked in 10% Sulfuric Acid (0.117 gm. H_2SO_4 per gram wool protein)				
3	60	250	21	2.15
9	60	250	20	2.13
12	60	250	21	2.19
21	60	250	20	2.30
30	60	250	8	3.90
40	60	250	3	4.75
50	60	250	1-2	5.92

*Specimens conditioned at a relative humidity of 65% and a temperature of 70° F.

more sensitive measure of the deterioration taking place during the baking process than decrease in breaking strength. This is evident from Table 4 in which samples treated with 2.5, 5.0, and 7.5 per cent sulfuric acid solutions and containing 3 per cent moisture showed no decrease in tensile strength after baking but showed appreciable increases in ammonia nitrogen content. Both the physical and chemical breakdowns increase with increasing acid concentration in the specimen and increasing temperature in the baking oven. The deterioration takes place in the first few minutes of baking. This can be explained by the assumption that the moisture content drops below the critical value in the first few minutes of baking after which no further breakdown occurs.

(4) *Agents Which Influence the Deterioriation of Wool in Baking*

Specimens of the wool cloth were soaked in a five per cent solution of sulfuric acid for 3 hours at 22° C, centrifuged, and air dried. The cloth was cut into strips (6″ x 1″), and four strips were placed in each of four glass tubes (10″ x 1.5″) which had been drawn out at the ends. The four tubes were treated as follows:

1. Evacuated with a "Hyvac" pump for four hours and sealed.
2. Moist carbon dioxide (CO_2 bubbled through water) was passed through the tube for two hours. This tube was then sealed.
3. Same as (2) substituting oxygen for carbon dioxide.
4. Same as (2) substituting air for carbon dioxide.

The tubes were placed in an oven at 250° F. for one hour. Similar experiments were made using untreated wool. The results given in table 5 indicate that both oxygen and moisture promote the deterioration of wool during baking. Sulfuric acid increases the deterioriation considerably.

(5) *Effect of Storage on the Dried Wool*

Specimens of the wool cloth were soaked in 2.5, 5.0, 7.5, and 10 per cent solutions of sulfuric acid for 3 hours at 22° C, centrifuged and stored in atmospheres of relative humidities of 6, 30, 65, and 90 per cent. They were exposed to a low intensity, incandescent light. At intervals of time, the ammonia nitrogen contents and breaking strengths were determined. The physical and chemical breakdowns of the specimens on storage are shown in Figures 3 and 4 respectively.

There is no evidence of any marked increasing physical breakdown of any of the acid-treated specimens on storage in atmospheres of 6, and 30 per cent relative humidities. The data suggest the possibility of some breakdown increasing with time of exposure with 90 per cent relative humidity using 5, 7.5, and 10 per cent solutions of sulfuric acid. The samples were weaker within 24 hours after treatment with acid than before treatment, this initial loss in strength being greater at the higher acid concentrations.

Table 5

The Effect of Baking on Untreated Specimens of Wool and Wool Treated with 5 Per Cent H_2SO_4 for 3 Hours at 22° C. in Vacuo and in Moisture Saturated Atmospheres

Atmosphere in tube	Appearance of Specimen		Breaking Strength 1 inch strip		Ammonia Nitrogen per gram of specimen	
	Treated	Untreated	Treated	Untreated	Treated	Untreated
			pounds	pounds	milligrams	milligrams
(1) Vacuum	Sl. Yellow	No change	21	27	6.4	.20
(2) Carbon Dioxide	Sl. Yellow	V. Sl. Yellow	15	26	10.5	1.29
(3) Oxygen	Dark Brown	Yellow	0	18	23.2	3.88
(4) Air	Yellow	V. Sl. Yellow	6	23	12.5	2.32

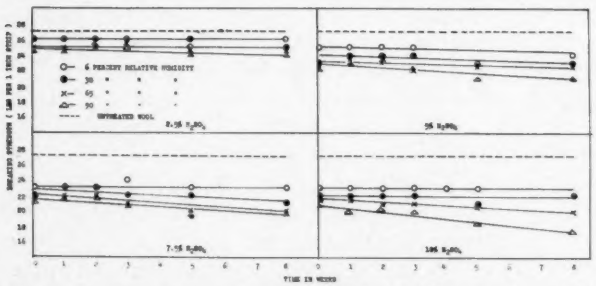

Fig. 3—The effect of storage at different relative humidities on the breaking strength of acid treated wool.

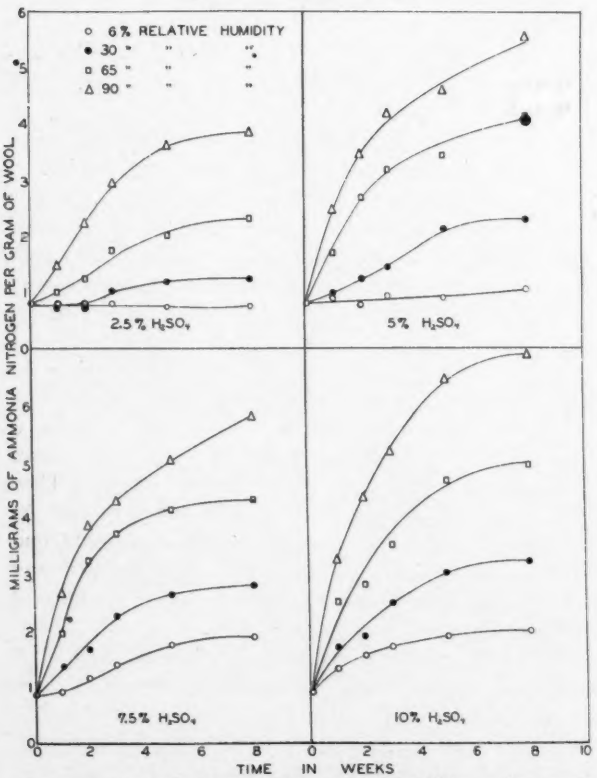

Fig. 4—The effect of storage at different relative humidities on the ammonia nitrogen content of acid treated wool.

With the exception of the specimens treated with 2.5 and 5 per cent solutions of sulfuric acid, and exposed to a relative humidity of 6 per cent, all of the specimens showed increasing ammonia nitrogen contents during storage. The ammonia nitrogen content increased with the increasing relative humidities, acid concentrations, and time of storage.

Here again it is shown that the ammonia nitrogen content gives a more sensitive measure of the deterioration taking place in the wool cloth than the breaking strength. That ammonia is found during protein deterioration is well known. Lloyd[6] states that ammonia is always released during protein hydrolysis, apparently from the acid amide groups. Leiben and Urban[7] studied the splitting of ammonia from amino acids and other substances and found the ammonia cleavage proceeds much more rapidly in acid than in an alkaline or neutral medium. In studying the photochemical decomposition of silk[8] the writer found that the deterioration was accompanied by the formation of ammonia and that the greatest amounts were formed in a given time in acid treated samples.

IV. Nature of the System Wool-Sulfuric Acid-Water

The reaction of sulfuric acid with wool depends on the chemical constitution and molecular organization of the wool protein. Sulfuric acid may be taken up and held by wool in three ways. First, it may be chemically combined, the combined acid being bound by primary valence forces at the free amino and imino groups and at the peptide linkages. Second, it may be absorbed at micellar interfaces and held by secondary valence forces. Third, it may be absorbed in capillary spaces in the wool fiber.

Considerable evidence has been presented for both the chemical type and adsorption type of combination of acids with proteins[9]. Additional evidence that at least some of the acid is chemically combined with the wool protein was obtained in a study on the absorption of iodine by wool[10]. The iodine number of wool is 14.1. After the wool is soaked in normal sulfuric acid the iodine number is only 2.6. On rinsing the acid treated wool in

[6]D. J. Lloyd, Chemistry of the Proteins, page 13, J. and A. Churchill (1926).

[7]F. Leiben and F. Urban. The Splitting of Ammonia from Amino Acids and Other Substances in the Light of a Quartz Lamp, Biochem. Z., vol. 239, pp. 250-6 (1931).

[8]Unpublished results.

[9]W. Hoffman and R. Gortner. Physico-Chemical Studies on Proteins, Colloid Symposium Monograph, vol. 2, pp. 209-368 (1925). The Chemical Catalog Company.

[10]Unpublished work by H. A. Neville, W. Fritz, and Milton Harris.

running water, the iodine number rises after one hour to 9.6 and remains at that value on continued rinsing. If an acid-treated specimen is first treated with a one per cent sodium carbonate solution to neutralize the acid and is then rinsed, the iodine number is the same as that of untreated wool. Since the iodine reacts with the free amino groups of the wool, the observations reported above indicate that the sulfuric acid combines with the free amino groups and occupies a place that would ordinarily be available to iodine. The combined acid is only removed by neutralization with alkali.

However, not all of the acid absorbed by the wool can be accounted for by assuming combination with the free amino groups. In Figure 2 it is shown that wool treated with 5 per cent sulfuric acid absorbs about one milli-equivalent of acid per gram of wool. Meunier and Rey[11] employing a modification of the Van Slyke apparatus found wool to contain 0.57 per cent of amino nitrogen. This would account for only 0.41 milli-equivalents of acid. Speakman and Hirst[12] using similar technique concluded that the amount of free amino nitrogen obtained from wool approached a limiting value of 0.92 per cent. This amount accounts for only 0.66 milli-equivalents of the acid.

That the amount of acid bound by the free amino groups of proteins does not account for the total acid taken up has long been known. Hitchcock[13] found that gelatin combined with 0.89 milli-equivalents of hydrochloric acid whereas deaminated gelatin combined with 0.44 milli-equivalents. Osborne[14] found that the amount of hydrochloric acid taken up by edestin was roughly five times the amount calculated on the basis of the amino groups. Sturin[15] neutralizes about 8 times as much acid as can be accounted for by the free amino groups.

It is evident that a large proportion of the acid absorbed by wool is not accounted for by its free amino nitrogen content. Several workers have shown that the residual combining capacity of proteins may be attributed to the peptide linkages[16, 17] and to the imino groups. It is probable that these groups also account for a portion of the acid in wool in excess of that necessary to react with the amino groups.

The absorption of moisture from the atmosphere by wool is, in general, very similar to the absorption of acids from solution. The amount of moisture absorbed depends upon the relative humidity; that is, the effective moisture concentration, whereas the amount of acid absorbed depends on the pH; that is, the effective hydrogen ion concentration. Both also depend on the physical and chemical nature of the specimen under consideration. Analogously to the way in which wool takes up acids, it is assumed that moisture may be taken up in three ways; namely, by chemical combination, by adsorption and by capillary condensation.

It is shown in Table 3 that wool treated with sulfuric acid absorbs less moisture than untreated wool. Evidence is presented above that sulfuric acid combines with the amino groups of wool. It seems logical to conclude that the difference observed in Column 4 of this table may be attributed either to combined sulfuric acid occupying places that would ordinarily be available to water, or that the combined and/or adsorbed acid has altered the forces capable of attracting the water.

Not all of the moisture taken up by the wool is combined or adsorbed, for if this were the case the two

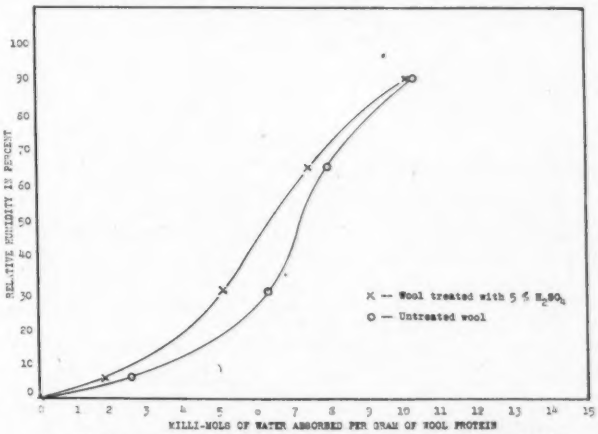
RELATIVE HUMIDITY IN PERCENT
MILLI-MOLS OF WATER ABSORBED PER GRAM OF WOOL PROTEIN
X — Wool treated with 5 % H_2SO_4
O — Untreated wool

Fig. 5—The absorption of water by untreated and acid treated wool.

curves shown in Figure 6 should lie parallel to each other. At the lower relative humidities the moisture may be taken up largely by adsorption and chemical combination and these processes occur simultaneously. At higher relative humidities the third process also occurs; namely, the capillary condensation of moisture. At very high relative humidities, for example 90 per cent, a large proportion of the moisture taken up is held by the capillary forces. Assuming that the acid in the wool has not changed the nature of these forces, both the acid treated and untreated specimens would take up like quantities of moisture by this process. This would account for the converging of the two curves. The curves for wool treated with higher concentrations of sulfuric acid may cross at the higher relative humidities because of the hygroscopic nature of the excess of sulfuric acid present.

[11] L. Meunier and G. Rey, "Sur Les Proprietes de la Laine," J. Soc. Leather Trade Chem., vol. 11, pp. 508-519 (1927).

[12] J. B. Speakman and M. C. Hirst. The Constitution of Keratin-Molecule. Trans. of the Faraday Soc., vol., 29, pp. 148-164 (1933).

[13] Hitchcock. The Combination of Deaminized Gelatin with Hydrochloric Acid. J. Gen. Physiol., vol. 6, pp. 95-104 and 457 (1923).

[14] T. B. Osborne. The Basic Character of the Protein Molecule, J. Am. Chem. Soc., vol. 24, pp. 39-78 (1902).

[15] A. Kossell and F. Weiss, Z. physiol. Chem., vol., 78, pp. 402-413 (1912). "Uber das Sturin."

[16] T. B. Osborne and C. S. Leavenworth. Protein Copper Compounds, J. Biol. Chem., vol. 28, p. 109 (1916).

[17] M. Siefried. Die Carbamino und Hydroxykohlensaurereaktion. Ergebnisse physiol., vol. 9, p. 334 (1910).

Proceedings of the American Association of Textile Chemists and Colorists

A Study of the Carbonizing Process and its effect on the Dyeing Properties of Wool

By BERTIL A. RYBERG[1,2]

Introduction

THE carbonizing process, the object of which is the removal of vegetable matter from wool, has been in use some fifty years. Despite its universal usage for so long a time, difficulties are being encountered daily in the woolen and worsted industry.

It was thought that a systematic study of the process from a practical viewpoint would be of value to the industry, in that any information obtained could be applied to the control of the process, thereby eliminating many of the difficulties usually encountered.

It is the purpose of this research to supply information and data on the carbonizing process and its effect on the dyeing properties of wool, to be used in the study of mill problems related to the carbonizing process.

The usual procedure for carbonizing wool cloth in the piece with sulfuric acid, is as follows:—

The goods are saturated in a 2% to 5% (3°-8° Tw.) solution of sulfuric acid, passing through squeeze rolls to ensure thorough saturation and the excess liquor is removed by a vacuum slot or by centrifuging. The material is dried at about 160°F. to 180°F. and baked at about 220°F to 230°F. The material is then dry milled to crush the charred burrs and then passes to the dyehouse, where it is rinsed or neutralized, dyed and wet-finished.

Carbonizing is also done using Aluminum Chloride as the carbonizing agent, but is not used on as large a scale as sulfuric acid, therefore an investigation of the sulfuric acid method will first be considered.

The materials used in this work consist of a high grade worsted cloth, with a plain weave, weighing 8 ozs. per running yard, and a typical 12 oz. woolen cloth containing small pieces of burrs. The worsted material is used in studying the effect of the various conditions on wool. The woolen material as a means of observing the conditions under which the vegetable material (burrs) is carbonized.

It is our purpose to duplicate mill conditions as nearly as our available equipment will permit in order that the information and data obtained will be of the greatest practical value to the industry.

EXPERIMENTAL WORK

1. The Effect of Temperature Variation in the Baking Chamber

A. A large number of samples of wool cloth containing small pieces of burrs were given a treatment as follows:

The samples were immersed for 15 mins. in a 4.25% (6° Tw.) solution of sulfuric acid (4.25 grs. H_2SO_4 per 100 c.c. solution) at room temperature (80° F.) and squeezed three times during immersion. Immersion for 15 mins. was selected as an average for practical work. After the final squeeze the samples were dried for 15 mins. at 160° F. to 170° F. in a semi-works dryer carbonizer, designed and built by the associate for this particular project. (Fig.. 1)

The dryer carbonizer was constructed in such a way that a good circulation of hot, dry air is maintained continuously. The ratio of the volume of hot, dry air to the amount of cloth being dried is large. In order to make the conditions as nearly ideal as possible, provision was made for the movement of the cloth samples. The samples 6" x 12" are fastened to the rotor by two corners and always hang in a vertical position when the rotor revolves. Contact with any part of the carbonizer occurs only at these points. The machine is heated by means of steam coils in the bottom of the chamber. Provision is also made for temperature control. Samples of wool cloth containing acid dried under these conditions for 15

[1] Research Associate for the American Association of Textile Chemists and Colorists at the Lowell Textile Institute.

[2] A Sub-Committee of the American Association of Textile Chemists and Colorists on the Carbonization of Wool, has acted in an advisory capacity in connection with this project. The committee is as follows: Roland E. Derby, Chairman, Hugh Christison, Harold Leitch, Claxton Monro, Alex. Morrison and Louis A. Olney.

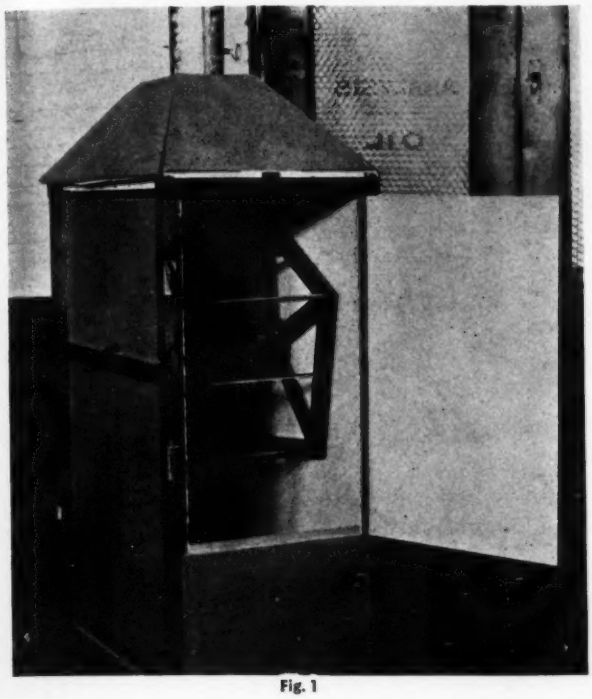

Fig. 1

mins. were thoroughly dried, that is in the ordinary sense of the word.

The dried samples were then baked 15 mins. at temperatures ranging from 210° F. to 250° F. (the usual range for commercial carbonizers), and then rinsed thoroughly.

Groups of the above samples containing uncarbonized wool material as well as carbonized, were dyed with 12 different typical acid dyestuffs. The dyeings were made using Glauber's salt only as an assistant. In practically all cases the affinity of the carbonized material for the dyestuffs was in direct relation to the temperature at which it had been carbonized. The higher the temperature of baking the less its affinity for acid dyestuffs. In all cases the uncarbonized material exhibited a greater affinity for the acid dyestuffs, then the carbonized, which shows that the carbonizing process apparently changes the dyeing properties of wool. The degree or amount of change being dependent upon the severity of the treatment.

B. Another group of samples were carbonized as above and neutralized with an excess of ammonia. They were rinsed and then dyed with several acid dyestuffs and the change in affinity for this type of dye seemed to be unaffected by the neutralizing treatment. Neutralizing with ammonia is usually done commercially when acid sensitive dyestuffs are to be used.

C. A group of samples carbonized as in A were dyed directly after carbonizing without removing the carbonizing acid. The decrease in affinity for acid dyestuffs was not nearly as noticeable, but the samples exhibited a mottled appearance. Many acid dyes cannot be suitably dyed in the presence of sulfuric acid of concentrations as great as occur on carbonized wool.

D. Samples treated as in A, B and C were dyed with a group of representative basic dyestuffs. In the case of basic dyestuffs the affinity of the wool for this class is increased by the carbonizing treatment and in direct relation to the severity of the treatment.

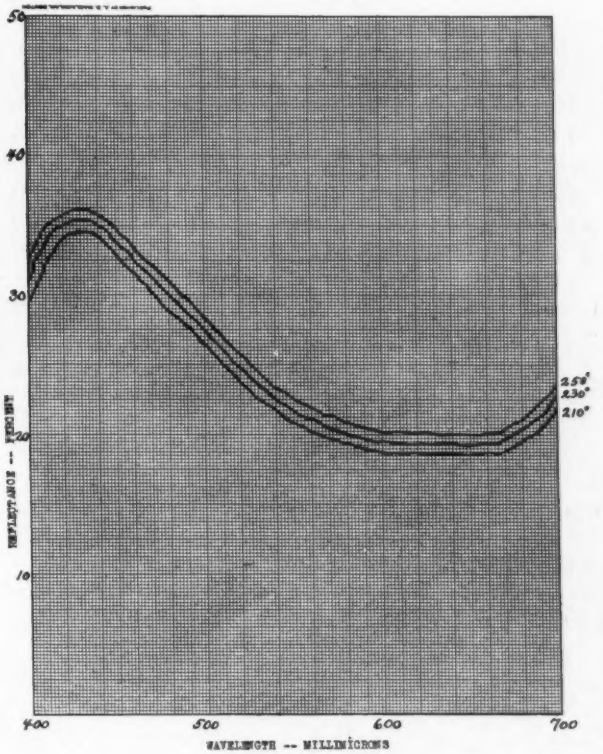

Fig. 2

E. The group of curves given in Fig. 2 represent the decrease in affinity for a typical acid dyestuff, Alizarine Saphirol B, Color Index No. 1054, caused by varying the baking temperature. These curves were obtained by means of a recording spectrophotometer[3] which measures the reflecting power of the dyed material. The material carbonized at the highest temperature (250° F.) exhibits the lowest affinity for acid dyestuffs, which means it has the greatest reflecting power. The topmost curve represents material carbonized at 250° F., the lowest curve 210° F., and that in between 230° F. These curves definitely show that there is a measurable difference in dye affinity which is in direct relation to the temperature of baking. However, this difference is small for large differences in temperature. A difference in shade can be seen between the extremes under proper lighting conditions.

[3]A. C. Hardy—A Recording Photo-electric Color Analyzer. J. Optical Soc. Am. & Rev. Scientific Instruments, Vol. 18, No. 2, Feb., 1929.

The spectrophometric measurements were made with the cooperation of Orrin W. Pineo, Senior Research Fellow for the Textile Foundation, located at the Massachusetts Institute of Technology.

F. It was thought that there might be a chemical reaction taking place between the wool and the acid under the physical conditions of the carbonizing process, which would explain the change in dyeing properties. Practically all protein deterioration is accompanied by a change in nitrogen distribution. The possibility of such a condition being brought about in carbonizing was investigated by making determinations of the ammonia nitrogen. The ammonia nitrogen is that nitrogen which is readily obtained by the distillation of the substance in question with weak alkaline solutions of Calcium or Magnesium Oxide. Ammonia nitrogen determinations were made on untreated wool, on wool carbonized at 210° F., 230° F., and 250° F., and thoroughly rinsed at room temperatures.

Results:

Untreated wool	.15 mg N/g wool
Wool, carbonized 210° F.....	.26 mg N/g wool
Wool, carbonized 230° F.....	.35 mg N/g wool
Wool, carbonized 250° F.....	.45 mg N/g wool

(Average of four determinations)

These results show that the carbonizing process brings about a change in nitrogen distribution, which may be an explanation of the decrease in affinity for acid dyestuffs and an increase in affinity for basic dyestuffs. Gerbhardt,[4] in his paper, "The Theory of Wool Dyeing," gives some interesting examples an explanations of how the dyeing properties of wool can be modified by various treatments.

2. The Effect of Time Variation in the Baking Chamber

A number of samples of the wool containing pieces of burrs, were given the usual immersion in acid solution, squeezing and drying treatment as given in Part 1. They were baked for varying periods of time, 5, 10, 15, 20, and 30 mins., at 220° F., then rinsed and dyed together with several acid and basic dyestuffs. A temperature of 220° F. was selected here since it is a temperature very commonly used in commercial work.

Results:

The longer the material was baked the lower its affinity for acid dyestuffs, and conversely the greater its affinity for basic dyestuffs.

The group of curves given in Fig. 3, represent the decrease in affinity for a typical acid dyestuff (Alizarine Saphirol B, C. I. 1054) caused by increasing the time of baking. These spectrophotometric curves are measures of the reflecting power of the samples tested. The upper curve represents 30 mins. carbonizing or baking, the center curve 15 mins., and the lower 5 mins. They show that there is a measurable difference in affinity for the acid dyestuff, this decrease in affinity being in direct relation to the time of baking. Here also, the difference in affinity for the acid dyestuff is small for comparatively large differences in time. The vegetable material appeared to be thoroughly carbonized in the first ten minutes of baking, in most cases, therefore the effect of increasing the time of baking is of minor importance.

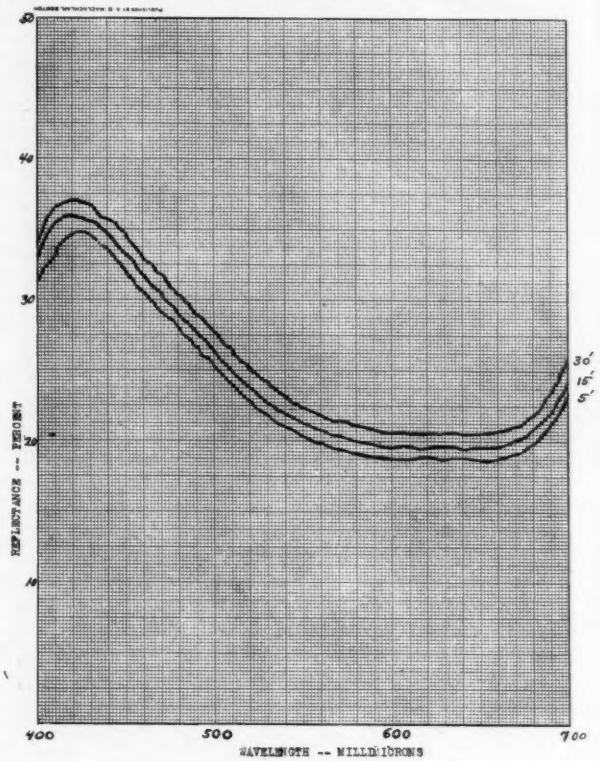

Fig. 3

Ammonia nitrogen determinations were made on a group of samples carbonized for varying lengths of time.

Results:

Untreated wool	.15 mg N/g wool
Wool carbonized 5 mins.....	.22 mg N/g wool
Wool carbonized 10 mins.....	.26 mg N/g wool
Wood carbonized 15 mins.....	.31 mg N/g wool
Wool carbonized 20 mins.....	.37 mg N/g wool
Wool carbonized 30 mins.....	.48 mg N/g wool

The date obtained indicates an increase in ammonia nitrogen with increasing time. These determinations are a more delicate measure of changes in composition than the difference in affinity for various dyestuffs.

3. The Effect of the Concentration of Sulfuric Acid in the Saturating Tank

Samples of the wool cloth containing pieces of burrs were immersed in acid baths ranging in concentration from 1% to 10% (grams/100 cc. solution) in intervals of 1%, for 15 mins. at 80° F. and squeezed three times during immersion. They were dried 15 mins. at 160° F.-

[4] K. Gerbhardt—The Theory of Wool Dyeing. Zeit, f. angew. Chem. p. 297 (1914). J. Soc. Dyers & Col., *30*, p. 284 (1914).

170° F., then baked 15 mins. at 220° F.-225° F. The samples were rinsed thoroughly, then dyed together with several typical acid and basic dyestuffs.

Basic dyestuffs on wool have practically no commercial value because of their poor fastness properties. Our reason for using them is that they act as an indicator of the change in dyeing properties of wool that has been corbonized.

The affinity for acid dyestuffs decreased with increase in concentration of the acid (sulfuric) in the saturating bath and the affinity for basic dyestuffs increased.

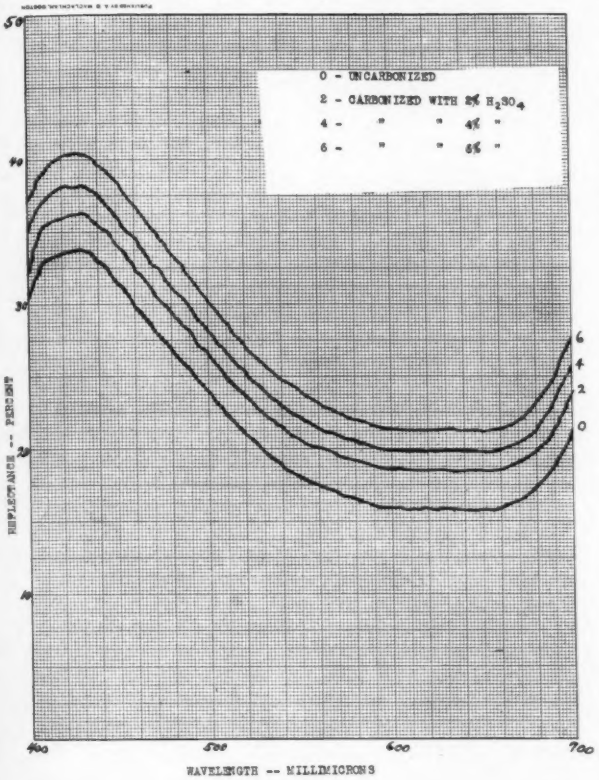

Fig. 4

The group of spectrophotometric curves given in Fig. 4, represent the decreasing affinity of carbonized wool for a typical acid dyestuff, Alizarine Saphirol B, C. I. 1054, caused by increasing the concentration of sulfuric acid in the saturating tank. They represent 0%, 2%, 4%, and 6% sulfuric acid in the bath (grams H_2SO_4 per 100 cc. solution), which cover the commercial range of acid concentrations most commonly used.

It can readily be seen that variations in the concentration of the acid in the saturating bath give quite pronounced changes in affinity for acid dyestuffs. These variations in the shade of the dyed material can easily be seen with the eye.

Ammonia nitrogen determinations were made on samples of wool cloth carbonized with various concentrations of sulfuric acid with the following results:

Untreated wool	.15 mg N/g wool
Carbonized with 2% H_2SO_4	.25 mg N/g wool
Carbonized with 4% H_2SO_4	.34 mg N/g wool
Carbonized with 6% H_2SO_4	.47 mg N/g wool
Carbonized with 8% H_2SO_4	.58 mg N/g wool
Carbonized with 10% H_2SO_4	.67 mg N/g wool

The data given indicates that an increase in the concentration of the sulfuric acid in the saturating bath is accompanied by an increase in the ammonia nitrogen.

The three variable factors, Time, Temperature in the baking chamber and Concentration of acid in the soaking bath influence the affinity of the wool for acid dyestuffs to a variable degree. It has been shown that concentration of acid in the saturating bath is the most important variable. Time is easily controlled as is also temperature, but concentration of acid in the wool is where the difficulty lies. The concentration of acid in the wool is dependent upon the concentration of acid in the soaking bath as can be seen by the following work.

4. The Effect of the Acid Concentration on the Absorption of Sulfuric Acid by Wool from the Saturating Bath

Acid saturating baths were made up in concentrations ranging from 0.1% to 1% in intervals of .1% and from 1% to 10% in intervals of 1% (grams sulfuric acid per 100 cc. solution). Samples of worsted cloth weighing approximately 4 grams were immersed for 15 mins. in 400 cc. portions of acid solution at 80° F., squeezed three times during immersion, weighed after extraction, and then transferred to flasks containing known volumes of 0.1N triethanolamine. The method used for determining the amount of acid taken up, is the Triethanolamine Method of S. R. Trotman and G. N. Gee.[5]

The results obtained are given in the absorption curve, Fig. 5, which represents the amount of acid (H_2SO_4) taken up and retained by the wool after extraction to a point where the extracted material weighed two times as much as the original dry material. The position of this curve depends somewhat on the degree of extraction of the excess acid liquor. If the material is extracted to less than double its dry weight, the curve will be slightly lower than that given in Fig. 5; if extracted to more than double its dry weight, it will be slightly higher, but in all cases the general shape of the curve will be the same.

5. The Effect of the Degree of Extraction Upon the Amount of Acid Absorbed and Retained by Wool

Weighed samples of worsted cloth were immersed in a 5% solution of sulfuric acid, squeezed three times and then extracted in the following way:

Group 1. Extracted by squeeze rolls to double its dry weight.

Group 2. Extracted to 1½ times its dry weight, by using a centrifugal extractor.

[5] S. R. Trotman and G. N. Gee—Determination of Acids in Wool with Particular Reference to Dyed Goods. Am. Dyestuff Reptr., *22*, p. 303 (1933).

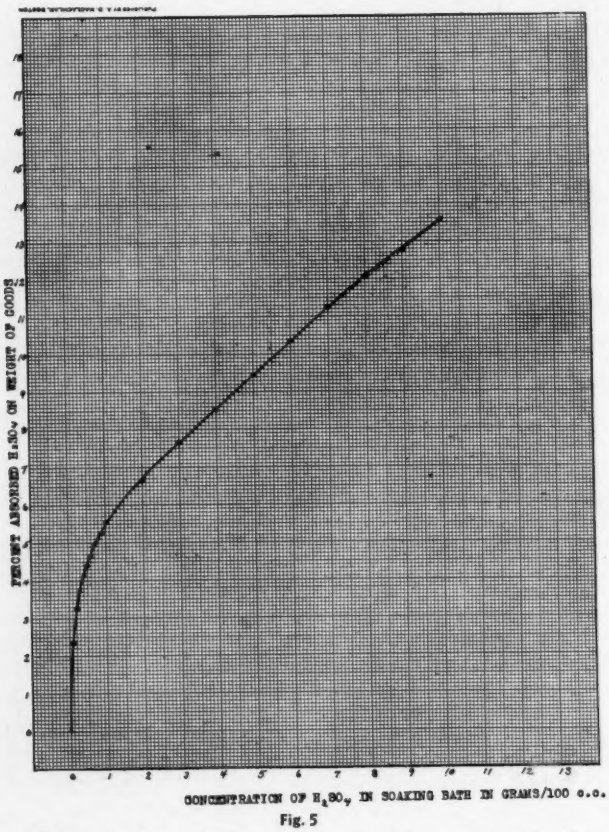

Fig. 5

Determination of the amount of acid remaining in the wool after extraction gave the following results:

Group 1	9.57% H_2SO_4
Group 2	7.90% H_2SO_4

(Average of three determinations)

This data indicates that the so-called mechanically held excess acid is not as important as is commonly thought. The amount so held is comparatively small as compared to the total.

Since the Triethanolamine Method of Trotman and Gee[5] is a comparatively new method for determining acids in wool, it was considered advisable to check it against the well known and accepted Terephthalic Acid Method of Hirst and King.[6]

Results:

H_2SO_4 by Terephthalic Acid	8.65%	
H_2SO_4 Triethanolamine		9.14%
H_2SO_4 Residual	.52%	.05%
H_2SO_4 Total	9.17%	9.19%

(Average of four determinations)

Residual sulfuric acid is that acid obtained by digesting the wool used in the above determinations with a 5% caustic soda solution, acidifying with hydrochloric acid, adding barium chloride, digesting again, filtering, washing and ashing. According to the results obtained, the Triethanolamine method yields results much nearer to the true acid content than does the Terephthalic Acid method. It therefore will be used whenever any further acid determinations are necessary.

[6]H. R. Hirst and A. T. King—The Estimation of Sulfuric Acid in Wool. J. Text. Inst., *27*, T101-3 (1926).

6. The Effect of the Initial Moisture Content of Wool on Its Absorption of Sulfuric Acid from Dilute Solutions

Samples of the worsted cloth of varying moisture content ranging from 6% to 20%, calculated as regain moisture, were immersed for 15 mins. in a 5% (5 grs. H_2SO_4/100 cc. solution) solution of sulfuric acid at 80° F., squeezed three times during immersion and the acid absorbed determined by the Triethanolamine method.

The results indicate that for a given length of time wool containing the greater initial moisture tends to absorb acid slightly faster than wool of low initial moisture, but that the actual amounts of acid taken up vary so little between the limits selected, that such small differences would not affect the dyeing properties enough to be measurable.

7. The Effect of Increasing the Temperature of the Acid Bath on the Absorption of Sulfuric Acid by Wool

Samples of the worsted cloth weighing 4 grams each, were immersed for 15 mins. in 400 cc. portions of a 2.5% solution of sulfuric at temperatures varying from 80° F. to 120° F. They were squeezed twice during immersion, then given a final squeeze, transferred to flasks containing known amounts of 0.1N Triethanolamine and allowed to stand over night. Determinations of the acid absorbed by this method gave the following results:

2.5% H_2SO_4 Solution

Time	Temp.	% H_2SO_4 Absorbed
15 mins.	80° F.	6.78
15 mins.	90° F.	7.02
15 mins.	100° F.	7.04
15 mins.	110° F.	7.07
15 mins.	120° F.	7.10

Average of two determinations.

The above determinations were repeated using a 4.5% solution of sulfuric acid.

4.5% H_2SO_4 Solution

15 mins.	71° F.	8.82
15 mins.	82° F.	9.08
15 mins.	90° F.	9.14
15 mins.	100° F.	9.12
15 mins.	110° F.	9.15
15 mins.	120° F.	9.14
15 mins.	130° F.	9.19
15 mins.	140° F.	9.30

Average of three determinations.

The results obtained indicate that there is a slight in-

crease in the amount of acid absorbed with increase in temperature for the given length of time.

8. The Effect of Wetting Agents on the Absorption of Sulfuric Acid by Wool from Dilute Solutions

According to the literature given by various manufacturers of wetting agents, there are very few wetting agents which retain their wetting power in acid solutions of carbonizing strength. The sulfated as well as the sulfonated fatty alcohols have no appreciable value in wetting wool with acid solutions. This was checked by testing various of these compounds under acid conditions such as met with in carbonizing.

Neville, Jeanson and Smith[7] state that the newer types of wetting agents, namely sulfated fatty alcohols and sulfonates of condensation products are so strongly absorbed by wool from solutions of high acidity that they can hardly be employed economically under these conditions.

The only type of wetting agent recommended by the manufacturers as suitable for carbonizing, is the naphthalene sulfonic acid type. Wetting agents of the naphthalene sulfonic acid type from two different manufacturers were used in the following work. Various concentrations of these wetting agents were tried in a 5% solution of sulfuric acid. A ½% solution of these agents in 5% sulfuric acid gave practically instantaneous wetting, that is within a maximum of 3 secs.

Exactly 4 gram samples of the worsted cloth were immersed in 200 cc. portions of a 5% solution of sulfuric acid at room temperatures (80° F.). The acid solution alone was used for one group, a 0.5% of a wetting agent (naphthalene sulfonic acid type) was added to the acid solution for the other group. (1 gram wetting agent in 200 cc. solution). The first group was squeezed twice during immersion and then given a final squeeze. The second group was squeezed once only to remove the excess acid liquor. The acid absorbed was determined by the Triethanolamine method. The samples were immersed for varying periods of time in order to observe the effect of the wetting agent on the rate of absorption.

Results:

	% H_2SO_4 Absorbed	
Time	Ordinary	Wetting Agent
3 mins.	8.21	7.97
6 mins.	8.69	8.42
10 mins.	8.74	8.83
15 mins.	9.35	9.44

The experiment was repeated using a wetting agent from a different manufacturer.

[7]H. A. Neville, C. A. Jeanson and A. L. Smith—Wetting Agents in Textile Processing. Am. Dyestuff Reptr., *22*, p. 565 (1933).

Results:

	% H_2SO_4 Absorbed	
Time	Ordinary	Wetting Agent
3 mins.	8.28	8.01
6 mins.	8.69	8.35
10 mins.	8.76	8.80
15 mins.	9.34	9.48

This type of wetting agent is absorbed slightly by the wool fiber, according to the literature of the manufacturers, but not nearly as much as the sulfated and sulfonated fatty or higher alcohols. Wetting agents are said to be more efficient when they are not absorbed.

The above data applies only to the effect of wetting agents on wool. It is proposed to determine the effect of wetting agents on burrs at a later date.

9. The Effect of Wetting Agents in the Acid Bath on the Dyeing Properties of Carbonized Wool

Samples of the worsted cloth were immersed in 5% solutions of sulfuric acid at room temperature for 15 mins. Group one was immersed in a plain acid solution, group two in an acid solution containing 0.5% of a wetting agent (naphthalene sulfonic acid type). Group one was squeezed three times during immersion, group two only once. They were then dried, baked, rinsed and dyed under the same conditions. Examination of the dyed samples showed apparently no perceptible difference in the shade or color depth. This was expected since the data in the preceding section showed such a small difference in the amount of acid absorbed for the time of immersion selected, using a wetting agent in one case and none in the other.

10. The Effect of the Method and Degree of Extraction of the Excess Acid Liquor

The common methods used today in removing the excess acid liquor from cloth previous to drying and baking are:—

1. Heavy Squeeze Rolls.
2. Squeeze Rolls plus Hydro-extraction in a Centrifuge.
3. Squeeze Rolls plus a Vacuum Slot.

Number one is seldom used alone, number two is used very much especially on the older types of carbonizers. Number three is used on the newer types of carbonizers and makes it possible to run the entire carbonizing range continuously.

Difficulties are often encountered in the use of a hydro-extractor (centrifuge). So-called resist markings sometimes appear which show an outline of the inside of the basket, particularly the holes through which the excess acid solution passes.

Samples of the worsted cloth were immersed in a 5% solution of sulfuric acid, squeezed three times during immersion, and further extracted in a laboratory centrifuge for varying periods of time and at varying speeds.

The samples were then dried, baked, rinsed and dyed under the same conditions.

Results:

So-called resist spots or markings were formed at the higher speeds and also the longer periods of time. The degree of resistance to dyeing increased with increasing time and speed. An outline of the inside of the basket which came in contact with the material during extraction could be clearly seen when the higher speeds were used. The unaffected portions of the material extracted at the higher speeds were dyed slightly deeper than those extracted at low speeds. The contrast between the resist markings and the unresisted portions was greater however, at the higher speeds. These resist markings apparently are caused by a greater concentration of acid at those particular places than in the rest of the material. It is suggested that there is a migration of acid to these particular places since they are situated on the outer edge of the bulk of the material directly against the sides of the basket, where the centrifugal force is the greatest. This tends to force the acid to the outermost circumference, therefore the excess acid from the bulk of the material must pass through the material which is in contact with the basket, which allows it to absorb more acid than the rest of the material.

Insufficient extraction is also dangerous since it allows an excess of acid and moisture to remain in the material which is liable to cause tendering and general resistance to dyeing. Uneven loading of the extractor causing it to wobble badly will slow it down giving insufficient and uneven extraction. This would probably result in cloudy or shady dyeings.

Squeeze rolls plus a vacuum slot as is used on the more modern carbonizers have the advantage of continuous operation in the open width. Difficulties are often encountered in using the vacuum slot. If the material is allowed to stop even for only a moment, a resist bar will invariably appear after dyeing, this being caused by the vacuum slot. There has been considerable controversy regarding the specific action of the slot in causing the so-called resist.

The following experiments were made in an attempt to explain the mechanism of the phenomenon.

Samples of the worsted cloth were immersed in a 5% solution of sulfuric acid and squeezed three times during immersion in order to ensure even and thorough saturation. Portions of these samples were further extracted in varying degrees by means of a glass tube and vacuum pump. They were then dried, baked, rinsed and dyed.

Results:

So-called resist spots were quite evident on the dyed material. Their intensity increased with increasing vacuum extraction.

Other samples were immersed and saturated as usual and portions of these were further extracted by means of a vacuum pump. The acid content of the extracted portion and of the neighboring unextracted portions were determined by the usual method.

Results:

The concentration of sulfuric acid was greater in the vacuum extracted than in the neighboring portions. It has been shown in part three of this paper that concentration of acid in the cloth is very important: that small differences in concentration will cause noticeable differences in dye affinity. It is our suggestion that a resist bar caused by over-extraction with the vacuum slot, is due to the acid migrating from the adjoining portions of the material to that being extracted, bringing about a greater concentration of sulfuric acid at that particular place. Continued extraction removes water but very little acid from the material, allowing the acid to accumulate and increase in concentration which in turn causes a corresponding decrease in affinity for acid dyes at that particular place when carbonized. Water is quite easily vaporized when a strong vacuum exists, whereas sulfuric acid is not appreciably vaporized by a vacuum at ordinary temperatures.

11. The Effect of Temperature Variation During the Drying Process

Samples of the worsted cloth were immersed in a 5% solution of sulfuric acid and squeezed as usual. These were dried for 15 mins. at temperatures varying from 150° F. to 220° F. in a small electric drying oven. They were then baked, rinsed and dyed under the same conditions.

Examination of the dyed samples showed that increasing the temperature of drying brought about a corresponding decrease in affinity for acid dyestuffs.

Samples immersed and saturated as usual, in some cases hydro-extracted at high speed, in others partly vacuum extracted were dried at temperatures varying from 150° F. to 220° F. They were baked, rinsed and dyed together.

Again the effect of increasing the temperature was noticeable. The resist spots and bars were more noticeable at higher temperatures of drying. These results indicate that drying at low temperatures 160° F. to 170° F. is advisable.

The following experiments were carried out in order to further substantiate the conclusion that proper drying is one of the most important phases of the carbonizing process.

Samples of the worsted cloth were immersed and saturated as usual. They were dried for 15 mins. at temperatures varying from 150° F. to 220° F. In drying the samples were folded in various ways so as to cause uneven drying. They were baked, rinsed and dyed together. (Dyeing in the majority of the experiments was

done using 1% Alizarine Saphirol B, C. I. 1054, a typical acid dyestuff, 20½ Glauber's salt crystals. Bring to a boil in 15 min., boil one hour.)

The effect of uneven drying was very noticeable resulting in uneven dyeing. The folded condition of the samples in drying was clearly shown in light and dark sections. The light portions being so-called resist spots. The resisted portions became more pronounced with increasing temperatures of drying.

Other samples of worsted cloth immersed and saturated as usual, were dried as uniformly as possible at 160° F. to 170° F. for 15 mins. They were then baked at 230° F. for 10 mins. In baking the samples were folded in various ways so as to cause uneven baking. They were rinsed and dyed together as usual.

The samples in all but one or two cases were dyed evenly. The exceptions were very slightly uneven, hardly noticeable. These results further indicate that the drying stage is probably the most important stage in carbonizing. Defects caused by improper drying are naturally made worse in subsequent baking.

The above experiments were repeated, using the dryer carbonizer built for this particular project by the associate. This semi-works carbonizer Fig. 1 gave quite different results from those obtained when using the electric drying oven. It was practically impossible to produce resist spots in this machine by the means employed for the laboratory oven. Since the same temperatures of drying were used in both cases, it was concluded that the speed of drying was the important part of the drying stage. The semi-works carbonizer is provided with a continuous flow of dry air at the proper temperature, and the volume of air is large compared to the amount of material being dried. These conditions promote rapid drying at the lower temperatures. Since the object of drying is the removal of moisture, it is evident that the moisture content of the material entering the dryer, the relative humidity of the air in the dryer and the rate of flow of the air through the dryer govern the efficiency of the drying operation as well as the temperature.

12. The Effect of Relative Humidity in the Drying Stage of the Carbonizing Process

Samples of the worsted cloth were immersed in a 5% solution of sulfuric acid and saturated as usual. They were dried at 160° F. to 170° F. for 15 mins. under varying relative humidities, in a small electric oven. The variation in relative humidity was effected by increasing the number of samples in the oven at any one time as follows:—

a. 1 Sample dried alone.
b. 2 Samples dried together.
c. 3 Samples dried together.
d. 4 Samples dried together.
e. 5 Samples dried together.

These samples were then baked at 230° F., rinsed and dyed under the same conditions.

Results:

a. Evenly dyed.
b. Very slightly lighter than a.
c. Slightly lighter than a.
d. Noticeably lighter than a. Also slight unevenness.
e. Very noticeably lighter, somewhat unevenly dyed. (Samples not thoroughly dried in 15 mins.)

The above experiments were repeated, drying at 185° F. to 190° F. The unevenness and loss of affinity for acid dyes was more pronounced than at the lower temperature. These results indicate that moisture is a very important factor in carbonizing.

Other samples saturated with acid solution as usual were hydro-extracted at high speeds and still others were partly vacuum extracted. These were dried under varying relative humidities, then baked, rinsed and dyed. Here again the influence of moisture was very noticeable. The contrast between the so-called resist spots and the body of the samples increased with increasing relative humidity.

These data indicate that material containing carbonizing liquor, if dried too slowly, or if it contains excessive moisture when entering the dryer will no doubt result in poor dyeing and in extreme cases tendered goods, especially if the dryer is being operated at high temperatures. (190° F. to 210° F.)

Ideal conditions for carbonizing based on the above findings would be:—

1. Material entering dryer contains a minimum of moisture.
2. Dryer should *not* be above 170° F. if a closed type and should have a large flow of dry air. The relative humidity of the air entering and leaving the dryer should be kept low in order to facilitate quick drying.

If the dryer is of the open type, higher temperatures are permissible, since such a dryer would have a considerable flow of air with a low moisture content. This, striking the material and passing through will carry the moisture away from it bringing about rapid drying. The rapid evaporation of the moisture of course tends to keep the material from getting dangerously hot while it still contains appreciable amounts of moisture. Complete removal of moisture from the material before it reaches the higher or baking temperatures is quite essential to proper carbonizing. The temperature, relative humidity and rate of flow of the air in the dryer are all variables which should be controlled and kept at the ideal operating condition during carbonizing. These of course will vary according to the type of material being carbonized.

The fact that it was practically impossible to produce

resist spots or markings in the semi-works carbonizer (Fig. 1) even with high drying temperatures is further proof that rapid removal of moisture will prevent the majority of the troubles usually encountered in commercial carbonizing. It is the combination of moisture and high temperatures which cause most difficulties.

13. The Effect of Relative Humidity in Baking

The relative humidity in the baker should be kept low for the same reason as in the dryer. The relative humidity of course, decreases with increase in temperature if no more moisture is allowed to be taken up by the air.

14. The Effect of Light (Daylight) on Wool Containing Sulfuric Acid

Samples of the worsted cloth were immersed in a 4% solution of sulfuric acid, (a concentration commonly used in commercial work) for 15 mins. and squeezed three times during immersion. They were dried at 160° F. to 170° F. for 15 mins., then baked for 15 mins. at 225° F. to 230° F. One group of these samples was then exposed to north daylight for varying periods of time and the other group was kept in a dark cupboard. Ammonia nitrogen determinations were made from time to time on both groups.

Results:

Untreated wool	.16 mg N/g wool
Carbonized & neutralized (Soda Ash)	.35 mg N/g wool
Carbonized & *unexposed* 1 week....	.39 mg N/g wool
Carbonized & *unexposed* 2 weeks...	.43 mg N/g wool
Carbonized & *unexposed* 4 weeks...	.51 mg N/g wool
Carbonized & *unexposed* 5 weeks...	.54 mg N/g wool
Carbonized & *exposed* 1 week.....	.68 mg N/g wool
Carbonized & *exposed* 2 weeks.....	.82 mg N/g wool
Carbonized & *exposed* 4 weeks.....	1.07 mg N/g wool

It is evident from the results obtained, that daylight accelerates the deterioration of wool containing sulfuric acid. The wool also deteriorates on storage away from daylight but not nearly as much as when exposed.

The material in the foregoing experiments contained only a small amount of moisture, about 8.5% calculated as regain moisture. The material was exposed under these conditions of low moisture content. Since a measurable deterioration took place at a low moisture content, which depends on the relative humidity of the surrounding atmosphere, it is quite probable that the rate of deterioration would increase considerably with a large increase in relative humidity or moisture content. This suggestion is based on the fact that an increase in moisture content during drying and baking is accompanied by an increase in deterioration, as shown in part 12 of this paper.

Samples of worsted cloth immersed and extracted as usual were exposed to daylight. Others were stored in a dark cupboard. Ammonia nitrogen determinations made from time to time indicate that wool containing acid before carbonizing deteriorates upon storage. Exposure to light accelerates the deterioration considerably.

In commercial carbonizing, precautions are generally taken to prevent material containing sulfuric acid either before or after carbonizing, from coming in contact with sunlight or strong daylight. It is an established fact that sunlight striking wool material containing sulfuric acid will cause a decrease in affinity for acid dyestuffs wherever the material was struck by the light.

Samples of wool cloth containing sulfuric acid were exposed to direct sunlight for varying periods of time. Ammonia nitrogen determinations were made from time to time on the exposed material.

Results:

Untreated wool	.16 mg N/g wool
Exposed to sunlight 1 week.....	.54 mg N/g wool
Exposed to sunlight 2 weeks.....	.93 mg N/g wool
Exposed to sunlight 4 weeks.....	1.78 mg N/g wool
Exposed to sunlight 5 weeks.....	2.13 mg N/g wool

Wool material containing sulfuric acid was also exposed to the light from a Fadeometer. Here again the deterioration of the wool was accelerated considerably.

It has been shown in the preceding sections that a decrease in affinity for acid dyestuffs is accompanied by an increase in ammonia nitrogen.

Portions of samples of wool material containing sulfuric acid were exposed to direct sunlight for 1, 2, 3, 4, and 6 hours. They were then dried if necessary, baked, rinsed and dyed together.

The parts exposed exhibited a lower affinity for acid dyes than the unexposed. The contrast increased with time of exposure. There was a barely perceptible difference in shade for one hour exposure which became increasingly noticeable with time.

15. The Effect of Carbonizing on the Dyeing Properties or Affinity of Wool for the Classes of Dyes Most in Wool Dyeing

The classess of dyes most used in wool dyeing are:

1. Acid dyes.
2. Mordant acid.
3. Mordant.

1. It has already been demonstrated in this work that carbonizing causes a decrease in affinity for acid dyes.

2. Samples of the worsted cloth carbonized in the usual way were dyed together with untreated material, with several typical mordant acid dyestuffs. Here again carbonizing causes a decrease in affinity for this type of dyestuff. This was expected since mordant acid dyes have practically the same dyeing properties as acid dyes. Resist spots were produced just as easily with mordant acid dyes as with acid dyes. These two types of dyes can therefore be considered as one as far as their affinity for wool is concerned.

3. Samples of carbonized cloth were mordanted to-

gether with untreated material and then dyed together with typical mordant dyes. A decrease in affinity for mordant dyes was exhibited in much the same manner as with acid and mordant acid dyes.

Acid dyes were used in most of the work because of the time element. Dyeings with acid dyes can be made in much less time than with either of the other types of dyes. Since the other types exhibited practically the same decrease in affinity for carbonized wool, it was considered unnecessary to work with more than one class, as this would be indicative enough of any change in dyeing properties.

16. Ways in Which Resist Spots Are Formed

In the course of our work attempts were made to find ways for producing so-called resist spots. Investigation of the various phases of the carbonizing process explained why resist spots were formed.

Resist spots were formed in the following way:

1. Over-extraction with the vacuum slot. Explained in part 10.
2. Hydro-extraction at high speeds as well as uneven extraction. Also explained in part 10.
3. Slow and uneven drying. Explained in parts 10 and 11.
4. Various conditions which might cause an uneven distribution of acid.
5. Sweating or condensation in the baker and dryer allowing moisture to strike the hot cloth.
6. Sunlight striking the cloth containing acid.

There are no doubt numerous other conditions which would cause resist spots to be formed in carbonizing. It is our belief that the information contained in this paper will offer a means toward solving, adjusting or eliminating any conditions which might cause trouble in carbonizing.

Summary

This research has shown that the dyeing properties of wool are affected by the carbonizing process. It also causes a deterioration of the wool itself. The following conclusions drawn from our work, show the effect on wool of the various stages of the carbonizing process.

1. Increasing the baking temperature results in a corresponding decrease in affinity for acid dyes and an increase in affinity for basic dyes. The decrease in affinity for acid dyes is comparatively small for moderate increases in temperature. Carbonized wool has a lower affinity for acid dyes than uncarbonized wool when dyed together. Neutralizing with ammonia after carbonizing has apparently no effect on the change in dye affinity.

Spectrophotometric curves showing the decrease in affinity for acid dyes caused by raising the temperature of baking are given.

Ammonia nitrogen determinations indicate that there is a chemical reaction between the acid and the wool, by exhibiting an increase in ammonia nitrogen after carbonizing, which increased further with increasing temperatures of baking.

2. It is shown that the time of baking is a variable. An increase in the time of baking results in a corresponding decrease in affinity for acid dyes and an increase in affinity for basic dyes.

Spectrophotometric curves are given which show the effect of time of baking on the affinity for acid dyes.

Ammonia nitrogen determinations indicate an increase in ammonia nitrogen with increase in time of baking. The Ammonia nitrogen is a better measure quantitatively, of the deterioration of wool than the change in dyeing properties.

3. The concentration of sulfuric acid in the material which depends upon the concentration of acid in the saturating bath and the method of extraction, is shown to be an important variable. An increase in concentration of sulfuric acid is accompanied by a decrease in affinity for acid dyes and an increase in affinity for basic dyes.

Spectrophotometric measurements indicate that a small increase in the concentration of acid results in a moderate decrease in affinity for acid dyes.

Ammonia nitrogen content increases with increasing concentration of acid.

It is shown that of the three variables, temperature and time of baking, and concentration of acid in bath, concentration is the most important. (Figs. 2, 3, 4.).

4. The relationship between the concentration of sulfuric acid in the saturating bath and the amount absorbed by wool for a given length of time and degree of extraction, was determined. A curve showing the relationship is given. (Fig. 5.)

5. The effect of the degree of extraction of acid liquor upon the amount retained by wool is given. Its influence on the total amount of acid held by the wool is not as important as is ordinarily thought.

6. The initial moisture content of wool in the lower ranges was found to have little or no effect on the absorption of sulfuric acid for a given length of time.

7. An increase in the temperature of the acid saturating bath results in a slight increase in the amount of acid absorbed for a given length of time.

8. Wetting agents have very little effect on the absorption of sulfuric acid by wool as compared to the absorption when squeeze rolls only are used. Only one type of wetting agent the naphthalene sulfonic acid type, will wet out wool satisfactorily in acid solutions of carbonizing strength. This conclusion applies to wool only, their effect on burrs will be taken up later.

9. Wetting agents suitable for carbonizing have apparently no effect on the dyeing properties of wool that is carbonized. No perceptible difference in the dyed ma-

terial, could be seen between material carbonized with and without a wetting agent.

10. The difficulties encountered in using hydro-extractors and vacuum slots for removing the excess acid were investigated. Conditions caused by these methods of extraction were reproduced and probable reasons for their occurrence are given.

11. The temperature of the dryer was found to be of considerable importance. Higher drying temperatures cause a correspondingly lower affinity for acid dyes. A comparison between the results obtained in a small electric laboratory oven and the semi-works carbonizer Fig. 1, indicate that the rate of drying is very important. The more quickly the material drys the smaller the change in dye affinity. Observations and results suggest that drying at low temperatures, 170° F. or below is advisable to insure minimum damage to the wool.

12. The effect of relative humidity of the air in the dryer as well as the moisture content of the material as it enters the dryer, is very noticeable. Experiments show that moisture is one of the most important factors in carbonizing. Quick, thorough drying at low temperatures is necessary in order to minimize the damage to the wool. The drying stage of the carbonizing process is the most important stage. Probably most of the damage caused in carbonizing can be traced to improper drying. If material is properly dried before baking, the chances of damage during baking are minimized. Moisture is necessary to most chemical reactions, therefore, the less moisture there is present, especially at the higher temperature, the less likely the wool is to be damaged. The quicker the moisture is removed the less opportunity it has to damage the wool. The fact that it was practically impossible to produce resist spots in the semi-works carbonizer, substantiates these conclusions, since drying conditions are ideal in this machine.

13. The relative humidity in the baker should be kept low for the same reason as in the dryer. The combination of moisture and heat is very injurious to wool containing sulfuric acid.

14. Daylight accelerates the rate of deterioration of wool containing sulfuric acid, as judged by ammonia nitrogen content. Direct sunlight accelerates the rate of deterioration considerably more than north light, and carbon arc light (Fade-Ometer) also accelerates the rate more than daylight alone. Wool containing sulfuric acid if stored in the dark will continue to deteriorate slowly. The accelerating effect of sunlight on the deterioration of wool containing sulfuric acid is great enough to cause a noticeable decrease in affinity for acid dyes in a comparatively short time.

15. The classes of dyes most commonly used in wool dyeing, namely—acid, mordant acid, and mordant all exhibit a decreased affinity for carbonized wool. Basic dyestuffs, which are of no commercial importance in wool dyeing, exhibit an increase in affinity. Since all three classes of commonly used dyes exhibited the same behavior toward carbonized wool, acid dyes were used in most of this work because of the time advantage in dyeing.

16. A partial list of ways in which resist spots are formed, is given.

It is our hope and belief that the information contained in this paper will offer a means towards eliminating the troublesome conditions encountered in commercial carbonizing.

Acknowledgement

This investigation was made possible by a grant from the Textile Foundation to the American Association of Textile Chemists and Colorists. We wish to express our appreciation for the aid given.

JUBILEE CELEBRATION
Society of Dyers and Colourists

The American Association of Textile Chemists and Colorists has received an invitation to send a representative to the jubilee celebrations of the Society of Dyers and Colourists.

These celebrations, to be held in Bradford, England, where the Society was founded, will begin on May 23rd with a civic welcome by the Lord Mayor of Bradford at the Technical College. The celebrations will continue until Saturday, May 26th, and will include visits to Bradford Technical College, Leeds University, the headquarters of the Wool Industries Research Association, and the works of Messrs. Isaac Holden & Sons, Ltd. A banquet will also be held as well as a civic reception by the Lord Mayor of York to be followed by a visit to places of interest in York.

Any member of the A.A.T.C.C. who plans to be in England at this time or who contemplates making the trip should communicate with President Robert E. Rose, P. O. Box 518, Wilmington, Delaware.

Proceedings of the American Association of Textile Chemists and Colorists

Review of

Carbonizing Project

By the SUB-COMMITTEE
ROLAND DERBY, *Chairman*

THE purpose of the two preceding research papers has been to determine certain fundamental facts by which we can account for the various troublesome results often produced on the woolen and worsted cloth which we process by the ordinary sulfuric acid carbonizing methods. With a reasonable understanding of these fundamentals we hope to be better able to control our process and more quickly solve problems which we meet.

The process as it has been carried out in the past has consisted generally of quite crude equipment and decidedly careless management. This was perfectly sufficient and satisfactory on stock dyed cloth, where the colors would stand the acid, as the effect on the wool was of no consequence unless it went so far as to tender the fibers appreciably.

As dyeing in the piece became increasingly popular and stocks were used which had not previously been carbonized, it became very advantageous to dye the stocks in the piece *after carbonizing*. Right here is where the difficulty started and the mills that ran into trouble did one of two things:—

1st. Changed to Aluminum Chloride Carbonizing.

2nd. Carbonized after dyeing.

These two alternatives have decided drawbacks; the Aluminum Chloride is 10 to 20 times more expensive than Sulfuric, and the goods carbonized after dyeing present the same troublesome resists and shades if they have to be redyed.

While a great many mills ran into extra difficulty with acid carbonizing *before* dyeing, others with apparently as crude equipment experienced no difficulty at all and without any change in their process, adopted the method of carbonizing before dyeing and seldom if ever had a resist spot or shady goods which could be attributed directly to the carbonizer. It can be readily seen that these mills had a very great advantage over mills in the other two groups.

The first step to remedy this has been the construction of continuous open width carbonizing equipment with vacuum extraction. This has nearly solved the problem because the engineers who have built these machines know many of the reasons for these troubles, and have built a machine which eliminates them (if handled according to their instructions) at a mere cost of $15,000 to $25,000. However even with this expensive equipment it is quite easily possible to make streaky, shady goods and to have just as bad resist spots as ever occurred in the worst old type machine, if they are not handled correctly.

In general it seems safe to say that the main reason for certain instances of apparent trouble-proof old type carbonizers was the use of an *open type dryer* or a dryer which gave *good circulation* of air and complete removal of water at low temperature before entering the baker.

It has often been assumed that the cause of resist spots was the deposition of metallic salts formed from the action of the acid on the metal parts of the saturating tank, the hydro-extractor, or guides in the dryer. This assumption was very logical because the actual shape of either the perforated basket or perhaps a can where the cloth turns in the dryer is left imprinted plainly on the cloth. However this is *not* from any metallic deposit but from uneven distribution of acid on the cloth and subsequent improper drying conditions.

Ryberg has shown that the concentration of acid has a very decided effect on the wool fiber. Now suppose we extract a piece of cloth unevenly, it seems reasonable to expect some variation in the effect of the acid on the cloth because as both Harris and Ryberg have shown the wool actually retains a protein of the acid. Hence the dry portions will start their carbonizing half way through the dryer (where the dryer is too hot) or the wet portions will not dry out (where the dryer has poor circulation).

However, the action of different concentrations of the acid in the cloth is minimized if not completely avoided

if the dryer has both low temperature and good circulation. Harris has shown that each concentration of acid has a critical moisture content where its action on the wool fiber at high temperature is greatest and also a point where it is not detrimental.

Another instance where the effect of metal has been erroneously blamed for the stains has been the pin marks on the selvage where a tenter dryer is used. The pins do build up a deposit of copper sulfate it is true, but it is not the salt which makes the resists, it is the retention of acid by this salt deposit and its marking off on the cloth just before entering the baker that makes the resist. Frequent washing with a solution of soda ash will keep this at a minimum. It is true that these pin marks can be made even when they are carefully cleaned. If this is the case, it is because the dryer is either *too cool* or has *poor circulation* and the metal parts carry away the heat so that the selvages are wet (even if they feel dry) going into the high temperature of the baker.

A typical example of this latter case is the marks of the dryer cans. If the cool, poor circulation condition exists and the cloth is stopped, the shape of the last can where the cloth lies against it can be seen. Let us say again right here that this is not because the metal has left a deposit or mordanted the cloth but because it has radiated heat which could not be used up in drying, and the moist acid saturated spot entered the high temperature of the baker and immediately reacted on the wool to make a spot which resisted the acid dye. In these cases increase in temperature of the dryer and improvement in its circulation will immediately stop all marks.

By improvement of circulation we mean more *removal of moisture,* not the recirculation of the same moisture laden air, but its *removal* and the entrance of *fresh dry warm air* to take its place.

The actual temperature where a dryer can be run safely is somewhat dependent on the conditions of moisture removal. If the dryer is so constructed that the moisture is carried away rapidly then the cloth can be run faster and a greater heat can be employed, say 180° F. If the circulation is poor then the temperature must be kept low, about 160° F., and the cloth pass through slowly so that it is completely dry before baking.

A good example of the *wrong* way to carbonize was shown in the experience of a well known New England mill. A carbonizer was constructed from an old dryer and in order to dry more quickly they decided to run the cloth into the top of the dryer first, where it was hottest. Since it was slightly inconvenient and expensive they did not provide any entrance for fresh air and only a small fan in one end of the dryer, which exhausted out doors. As it happened, the goods they were runing on at the time were all blacks or stock dyed so it seemed to work fine, and was lauded as being an economical success. Soon after, the spring line came in with a lot of fancy piece dyes and then they found out what resist spots looked like. Every piece carbonized was streaked and blotched after dyeing. No solution could be found until the carbonizer was rebuilt. The cloth was entered at the bottom where it was coolest, a fresh air duct was supplied and the exhaust pipe enlarged and taken from the top. All their troubles stopped at once.

Another mill experience which may be helpful is that experienced by a woolen mill on blow steamed and carbonized piece goods. The pieces were shaded side to center and during investigation the carbonizing was eliminated with the amazing result of reversing the shadiness. Instead of light sides and dark centers they now had dark sides and light centers. The sides were found to be oversteamed. This unevenness after dyeing can be accounted for because the over-steamed portions of cloth had increased affinity for acid. In the saturating tank of the carbonizer the excess acid absorbed was enough to resist the cloth in drying. In the dye bath the uncarbonized cloth absorbed more acid and hence more acid dye on the sides than the center.

Another common example of resist trouble is the line made by the vacuum slot when the open width carbonizer is stopped and the vacuum allowed to run. The water is, of course, dried right out of that portion of cloth resting over the slot. This goes into the dryer which is usually too hot and is immediately baked.

The moisture condition in the dryer gives a perfect chance for the reaction on the wool fiber with a resisted line as the result. Had the temperature of the dryer been low enough this line would not have been made.

The action of the acid on the wool is not always shown by marks or blotches after dyeing, but often by differences in shade side to center and very often end to end, showing that the acid concentration was uneven and that the dryer was unfit to rectify this condition. It is often possible to have a perfect piece and yet have that same piece resisted. It is only necessary to have it evenly resisted so that no part has more dye affinity than another.

The statement that a carbonized piece of cloth has less affinity for acid dye than an uncarbonized piece is often questioned and can be better explained in this way: Two pieces in the *same* dye bath, one uncarbonized and the other carbonized and with no acid in the dye bath, the uncarbonized cloth will dye darker with acid colors. However, these same two pieces in *separate* dye baths will be decidedly reversed. The reason is, of course, that the cloth containing the carbonizing acid liberates enough acid to dye the other piece, and under the same conditions the acid treated cloth has actually *less* affinity for the dye. Both Harris and Ryberg have shown this by several experiments.

One of the easiest ways to prove to ourselves that it is the action of different concentrations of acid under moist

conditions is to actually make a resist spot for ourselves. It can be done in the following way: Saturate with acid, and carefully dry at low temperature (160° F.) a small piece of cloth. Remove this cloth and mark the letter R or other design on it with the saturating acid and immediately put it into baking temperature of 240° F. The result after dyeing will be as shown in Fig. I. The same cloth carefully dried with the R resist mark on it before baking shows no resist after dyeing—Fig. II. Fig. III shows a similar test where the temperature was high but the circulation good. This interests further research because while there is no resist the silk is destroyed.

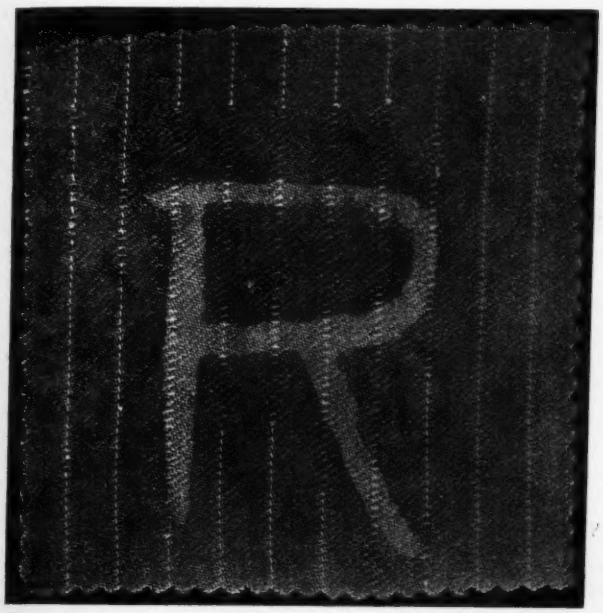

Fig. 1

A laboratory test of the radiation of heat of metal touching the cloth can be made by baking (240° F.) the wet acid saturated cloth as it lies on a metal screen or grid. The design of the grid will be perfectly shown after dyeing.

This cannot be done under low temperature and good circulating conditions. Ryberg in his work started out by constructing a practical laboratory carbonizer. He did a perfect piece of work, because he found that he could not produce any of the common faults which he wanted. Everything was even and without sign of resists. In order to produce the desired faults he had to resort to the laboratory drying oven.

In the research work on this subject certain fundamentals have been definitely proved by both Harris and Ryberg and for use in the industry these facts may be graphically represented as shown in Fig. IV and Fig. V.

Their individual work gives a more detailed description

Fig. 2

but for general purposes this figure represents the results, and if these changes are kept in mind every variable in the effect of sulfuric acid on wool can be accounted for.

The work of both research associates gives great opportunities for new developments and should be carefully considered. For instance, Harris gives a table of the effect of acid on wool in varied atmospheres and in vacuum, with comparative blank on untreated wool. The results under vacuum certainly show possibilities of a perfect

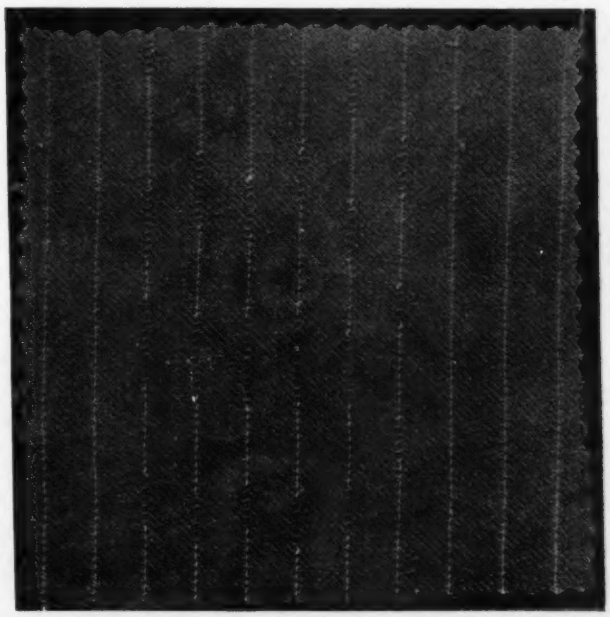

Fig. 3

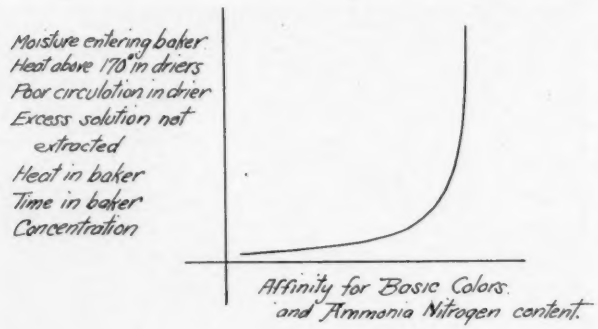

Fig. 4

dryer if it could be constructed under these conditions, where complete removal of water could be attained at ordinary or low temperature.

The ammonia nitrogen content has certainly been shown to be a close check on what happens between the wool and acid. No doubt mill chemists will make more use of this method in solving their carbonizing problems.

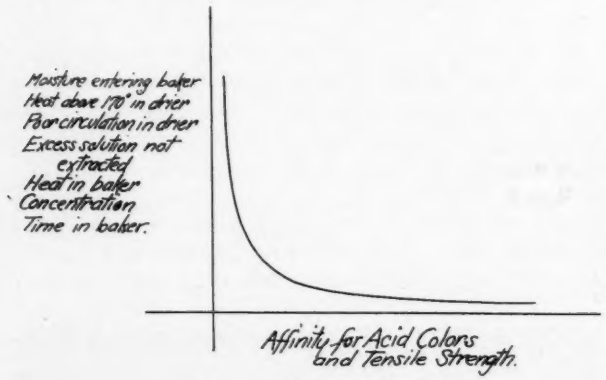

Fig. 5

The work of this research has left several loose ends which present interesting and valuable possibilities for future research. For instance, the slight variation in the results obtained by increasing the temperature of the soaking bath could be well investigated. The fact was discovered in the making of the resist spots that real silk effect threads were completely destroyed under conditions which had little or no effect on the wool. This might serve as a nucleus to some research along the lines of removing silk specks from wool shoddy, a welcome finding to many shoddy plants. See Fig. III.

No work has been done with Aluminum Chloride, and here certainly is a field for research to prove its value, if any, as compared to Sulfuric Acid. The same is true of Hydrochloric Acid gas carbonizing.

If this present work proves of interest to the trade, perhaps some future work can be carried out along these lines.

MEETING OF PHILADELPHIA SECTION

THE Philadelphia Section held a meeting, the third of the present season, on Friday, March 2nd, at the Penn Athletic Club, Philadelphia.

After the usual routine business, which included the appointment of a nominating committee who were requested to report to the next meeting, April 20th, their suggestions for elective officers to serve for the coming year, two prepared papers were presented.

The first by Mr. John T. Gibbons, director of research for the Joseph Bancroft & Sons Co., Wilmington, Delaware, entitled "The Preparation and Uses of Starch Products," and the second entitled "Haveg in the Textile Industry," by Mr. William H. Adams, Jr., technical director of the Haveg Corporation of Newark, Delaware, assisted by Mr. William E. H. Bell of W. H. Butterworth & Sons Company. The latter was illustrated by slides and numerous samples. Interesting discussions followed both papers.

The business meeting was preceded by the usual informal dinner. Attendance was 55.

Respectfully submitted,

CHARLES A. SEIBERT,
Secretary

NINETY-FOURTH COUNCIL MEETING

THE Council held its 94th meeting at the Bureau of Standards in Washington, on Friday afternoon, March 23rd. President Robert E. Rose presided. Also present were: William R. Moorhouse, Treasurer; Louis A. Olney, Chairman of the Research Committee; William D. Appel, Councilor-at-Large; Roland E. Derby, representing Northern New England; James Robert Bonnar, appointed to represent Rhode Island; Hans Meyer, representing New York; Harold B. Dohner, representing Philadelphia, and Harold C. Chapin, Secretary.

Regrets were received from Alex. Morrison, A. R. Thompson, Jr., W. M. Scott, D. H. Powers, H. F. Lawton, and E. F. Hempel.

The minutes of the 93rd meeting were approved as published. The Treasurer's report of March 20th, and the Secretary's balance sheet of March 21st, both attached hereto, were accepted.

Each of the following, approved by the Membership Committee, was elected to the class of membership specified, as of thirty days from publication of application, provided no objection be received before that date by the Secretary:

Active

William Beck, Harry Bentley, Joseph Corea, H. B. Dixon, Joseph H. Easley, Arthur W. Etchells, Irving E. Fairbrother, John F. Fitzgerald, Arthur L. Fowler, Jr., David Himmelfarb, Gilbert T. Latham, H. Davis Merion,

John Miller, Burton F. Mitchell, Francis B. Morton, C. W. Nichols, C. Norris Rabold, Herbert Seyferth, Harry M. Sprogell, Henry Weiss, Sidney L. Wheaton.

Junior

John H. Ciciva, Harold L. DeTurck, Peter S. Gilchrist, Jr., M. H. Mettee, 3rd, Raymond C. Warner.

Associate

Porter H. Brown, John Dempsey, W. E. H. Searcy, 3rd.

Student

Elliot F. Anderson, W. G. Faw, Hyman H. Greenbaum, B. R. Harris, Glen M. Kidder, Kenneth E. Leslie, Joseph A. Porter, Jr., Howard N. Stolzberg, E. M. Williams.

Ernest L. Caswell, A. K. Haynes, Robert L. Moore, and Clifford W. Sampson were transferred from Junior to Active membership; and Stanley E. Wojas from Student to Junior. Other names were referred to the Membership Committee.

It was voted that the Treasurer be empowered to transfer $2,000 temporarily from General to Research Fund, pending expected receipts specifically designated for research. To conform with certain banking formalities, it was further voted that the Treasurer be authorized to sign checks drawn on the funds of the Association on deposit with the First National Bank of Boston, and to transfer at his discretion, funds from the Savings Account to the Checking Account, or the Checking Account to the Savings Account.

A report was received from Henry F. Herrmann, Chairman of the New York Section, outlining plans for the Annual Meeting on December 7 and 8, in the Hotel New Yorker.

Respectfully submitted,

HAROLD C. CHAPIN,
Secretary

Treasurer's Report

MARCH 20, 1934

General Fund

Cash on hand—January 26, 1934	$9,107.93
Receipts—January 26, 1934, to March 20, 1934	1,512.40
	$10,620.33
Expenditures—January 26, 1934, to March 20, 1934	$695.73
Balance—March 20, 1934	$9,924.60

Research Fund

Cash on hand—January 26, 1934	$3,582.32
Receipts—January 26, 1934, to March 20, 1934	.....
	$3,582.32
Expenditures—January 26, 1934, to March 20, 1934	$1,775.27
Balance—March 20, 1934	$1,807.05

Bank Balance, March 20, 1934

General Fund	$9,924.60
Research Fund	1,807.05
	$11,731.65
First National Bank—Checking Account	$6,195.22
First National Bank—Savings Account	5,536.43
	$11,731.65

Respectfully submitted,

W. R. MOORHOUSE,
Treasurer

EIGHTY-SEVENTH RESEARCH COMMITTEE MEETING

THE 87th meeting of the Research Committee was held at the Bureau of Standards in Washington on March 23, 1934 with Dr. Louis A. Olney presiding.

The following members were present:—

W. D. Appel, R. Bonnar, H. D. Clayton, R. E. Derby, H. Meyer, W. R. Moorhouse, G. A. Moran, H. A. Neville, R. E. Rose, H. C. Chapin.

Regrets were received from:—

W. H. Cady, R. Hart, W. E. Hadley, B. L. Hathorne, E. F. Hempel, C. Monro, A. Morrison, D. H. Powers, W. M. Scott, A. R. Thompson, Jr., W. S. Williams.

Reporting for the Sub-Committee on Shrinkage, Mr. Clayton, Chairman, stated that progress was being made

Secretary's Balance Sheet

MARCH 21, 1934

	Applications	Dues, regular & reinstatement	Dues, sustaining & contributions	Dues Corporate	Miscellaneous	Totals
Received by both Secretaries, Nov. 1 to Jan. 25.	$177.50	$3,616.36	$220.00	$1,500.00	$108.64	$5,622.50
Received by Secretary, Jan. 25 to Mar. 21	222.50	1,004.15	35.00	.....	24.86	1,286.51
Receipts, total for fiscal year to March 21	400.00	4,620.51	255.00	1,500.00	133.50	6,909.01
Transmitted to Treasurer by both Secretaries	322.50	4,353.55	240.00	1,500.00	121.50	6,537.55
Leaving to order of Secretary in Appleton Bank of Lowell	77.50	266.96	15.00	.....	12.00	371.46

toward agreement on shrinkage tests between this Association, the American Society for Testing Materials, and the Federal Specifications Board.

Dr. Neville made a preliminary report on work with his students at Lehigh, in measuring the surface electrical charge on suspended cotton particles in various solutions.

Dr. Olney described the organization of the Sub-Committee on Mercerization in the South, having tentatively the following members:

Charles B. Ordway, Chairman; C. D. Brandt, E. A. Feimster, G. P. Feindel, E. R. Ford, A. H. Grimshaw, Mr. Grotte, C. A. Jones, A. J. Kelly, W. S. McNab, E. R. Manning, B. F. Mitchell, H. Schroeder, B. Smith, A. R. Thompson, Jr., Mr. Tillinghast, F. O. Tilson, W. Wohlar.

A report was accepted, for publication elsewhere in these Proceedings, on a meeting in New York on March 22 arranged by the International Silk Guild, and attended by Dr. Scott and the Secretary as representatives of this Association. At the request of the Silk Guild, Dr. Olney and Dr. Scott were appointed by the Research Committee as members of a group to give further consideration to Definitions and Standards for Silk.

Dr. Olney stated that the work of Dr. Harris and Mr. Ryberg on Carbonizing was about to be published. It was proposed that Mr. Ryberg continue this work; that Dr. Glarum continue his work on printing pastes. Dr. Harris outlined plans for a comprehensive investigation of the effect of alkalies on wool.

Mr. W. C. Smith described experiments which he is now conducting on comparative fading in different parts of the spectrum under varying conditions of exposure to light.

Mr. Derby further described plans for Mr. Ryberg's carbonizing investigation.

Mr. Appel called attention to recent Bureau of Standards Publications, LC-392 listing publications from the Bureau and its staff on Dyes, and LC-396 listing all publications on Textiles and methods of obtaining information from the Bureau of Standards.

Mr. W. E. Emley welcomed the group to the Bureau and invited attendance at a meeting of the U. S. Institute for Textile Research in New York the next day, to discuss Wear Tests on Fabrics.

HAROLD C. CHAPIN, *Secretary.*

SILK DEFINITIONS

A Joint Conference on Silk Definitions was held on invitation of the International Silk Guild in the Hotel New Yorker on Thursday, March 22nd, and was attended by representatives of the Bureau of Standards, American Association of Textile Chemists and Colorists, National Association of Hosiery Manufacturers, Institute of Dyers and Printers, Textle Converters Association of America, Federated Textile Industries, Inc., Silk Manufacturers' Association of Paterson. National Retail Dry Goods Association, Throwsters Research Institute, United States Testing Company.

Dr. Walter M. Scott and Dr. H. C. Chapin represented the American Association of Textile Chemists and Colorists.

President Paolino Gerli stated that the object of the Guild, in calling the meeting, was to protect silk, its good name and repute, enhance its value and desirability in the eyes of the public, and to do those things within the industry which will help to bring about these results; the first step being the establishment of definitions which would provide for silk articles a terminology simple, descriptive, and generally acceptable to the trade, and those representative bodies having to do with the consumers' interest.

Mr. D. E. Douty of the U. S. Testing Co. was introduced by Mr. Gerli as representative of the Guild and chairman of the meeting. Mr. C. J. Huber of the same company outlined the history of attempts in this country to restrict the percentage of weighting. J. E. Bell, also of U. S. Testing Co., presented a paper on "Development of Methods for Determining Weighting, with Suggested Basis for Calculating Percentage." William D. Appel described recent studies of weighting and silk deterioration made in the Bureau of Standards, showing that weighting was but one of the factors determining the durability of silk. H. A. Mereness of the Federated Textile Industries, Inc. (formerly the Silk Association of America), presented outlines of the present French standards for silk, the standards of the National Federation of Textiles, Inc., and a classification suggested by Mr. Douty as an outline for American standards.

In the general discussion, Horace Cheney of Cheney Brothers presented his opinion that the standards of the industry could best be improved through adoption of simple definitions, and enforced through legislation already existing and waiting to be invoked by the consumer.

Mr. Sweitzer of the National Retail Dry Goods Association believed that the consumer was becoming more conscious of differences in quality, and that the problem was to find what he wanted and give it to him so labelled that he could recognize it.

Dr. Scott and Mr. Friedman both stated that methods of analysis were now available for accurate classification of materials in at least three grades of weighting.

It was voted that the chairman appoint a committee to embody the suggestions offered, and others received subsequently by the International Silk Guild at 250 Fifth Ave., in more definite recommendations.

AMERICAN
DYESTUFF
REPORTER

LOUIS A. OLNEY, Sc.D.
Professor of Chemistry and Dyeing, Lowell Textile Institute
Directing Editor

NORMAN A. JOHNSON
Managing Editor

MYRON DREW REESER
Advertising Manager

Published biweekly by
HOWES PUBLISHING CO., INC.
440 Fourth Avenue, New York City

A. P. HOWES, President
M. D. REESER, Secretary
H. F. CRAWFORD, Treasurer

Subscription price: $5.00 per year; Canadian $6.80; foreign $6.00

Vol. XXIII April 23, 1934 No. 9

KNITTING ARTS EXHIBITION

TODAY marks the opening of the Thirtieth Annual Knitting Arts Exhibition now being held in the Commercial Arts Museum in Philadelphia. This exhibition has earned the reputation of being one of the most worthwhile annual trade events of its character and from present indications the show this year has surpassed that of last year in point of size and attendance.

The remarkable showing at this exhibition year after year seems to indicate that there is a real and definite reason for an annual exhibition of knitting machinery, accessories and supplies for the benefit of the manufacturing and processing trade.

Although primarily intended for the manufacturer, the many exhibits now showing which are directed toward the processing end of knit goods are of more than passing interest to the dyer, chemist and finisher.

If you have not already made plans to attend this exhibition it is still not too late to do so. The exhibition, although starting today will continue until Friday at 5 P. M. There are plenty of interesting and instructive exhibits to see and it will be well worth your while to come if it is at all possible.

For the benefit of the readers of this journal there follows a list of those exhibits which will probably be of particular interest to them.

AMERICAN ANILINE & EXTRACT CO.
Venango and F Streets
Philadelphia, Pa.
Booth No. 20

No products are exhibited but the booth will be used for reception purposes.

THE J. B. FORD SALES CO.
Wyandotte, Mich.
Booth No. 291

The products exhibited include a line of chemicals used in the bleaching, dyeing, and finishing of wool, cotton, silk and rayon fabrics. Those in attendance are F. S. Klebart (Wyandotte), James F. Flaherty (Boston), H. E. Moyer (Philadelphia) and John W. Turner (Philadelphia).

THE PHILADELPHIA DRYING MACH. CO.
3351 Stokley St.
Philadelphia, Pa.
Booth No. 182

The exhibit consists of illustrations of improved drying machinery for raw stock, skein and warp yarns, hosiery, underwear, toweling and piece goods. Also shown are tenter dryers, carbonizing equipment, vacuum extractors and electric drying forms. W. W. Sibson, H. O. Kaufman and C. H. Reuman are in attendance.

FRANKLIN PROCESS CO.
Providence, R. I.
Booth No. 222

Dyed and bleached yarns feature this exhibit. C. E. McElwee and G. E. MacGilivray are in attendance.

GRAND RAPIDS TEXTILE MACHINERY CO.
Grand Rapids, Mich.
Booth Nos. 161-162

Two new machines are exhibited for the first time in this booth. W. H. Shields and A. Stormzand are in attendance.

HYGROLIT, INC.
572 Davis Ave.
Kearny, N. J.
Booth Nos. 151-152

Two types of cone conditioning machinery are shown and demonstrations of the effects of liquid fluids, etc., are made. C. F. Dulken (President), R. A. Quack (Chief Engineer) and H. E. Kresse (Sales Manager) attend.

BAUSCH & LOMB OPTICAL CO.
Rochester, N. Y.
Booth Nos. 175-176

Optical instruments for the textile industry including textile projectors, wide field stereoscopic microscopes, textile laboratory microscopes, photomicrographic apparatus, fiber measuring apparatus, pick and course counters, etc., are exhibited. A special feature is the new simplified textile projector for

the study of all types of fabric defects. Visitors are invited to bring their own samples for inspection. The representatives present are W. H. Slocum, J. I. Wexlin and E. S. Bissell.

ONYX OIL & CHEMICAL CO

Jersey City, N. J.

Booth No. 341

Samples of various scouring, dyeing, and finishing compounds used on hosiery, underwear and other knit goods are featured. Actual samples processed with Onyx compounds are also shown. In attendance are J. W. Huber (Philadelphia), Charles E. Maher (Midwest), E. W. Klump (South), L. P. Brick (New England) and Charles D. Ehrengart (Secretary and General Sales Manager).

E. F. HOUGHTON & CO.

240 West Somerset St.

Philadelphia, Pa.

Booth Nos. 167-168

In addition to the showing of leathers and lubricating oils there are also exhibited new developments in textile oils and soaps including a new process for soaking and sizing rayon, new detergents for scouring rayon, cotton, silk and wool, new dye bath assistants and several new finishing oils. Among the many in attendance at this booth are found the following: Geo. W. Pressell (Director of Sales), Geo. S. Rogers (General Sales Manager), H. C. Roberts (Manager Textile Sales), Walter A. Buechner (Ass't General Sales Manager), V. W. Wells (Advertising Dept.) and H. J. Waldron (Southern Sales Manager).

INDUSTRIAL DRYER CORP.

Stamford, Conn.

Booth No. 154

The H-W Conditioner for conditioning silk on the cone and the H-W Holding Truck are shown at this booth. Those in attendance are George D. Millspaugh (Ind. Dryer Corp.) and Charles Kitmiller (Berks Eng. Co., agents.)

NYANZA COLOR & CHEMICAL CO.

215 Water St.

New York, N. Y.

Products exhibited are limited to recent additions to their line of specialties for the knit goods trade. The exhibit is in charge of P. C. Zell (Demonstrator) and also present are Louis Hoehm (Chicago), B. T. Leaver (Philadelphia), R. M. Town (Philadelphia), J. H. McNab (South) and representatives from the N. Y. office.

INTERNATIONAL NICKEL CO.

67 Wall Street

New York, N. Y.

Booth Nos. 13-14

This exhibit features mill and fabricated forms of Monel metal. Particular attention is given to the display of data and exhibits illustrative of the field of uses for Monel metal dyehouse equipment. Nickel-clad steel data and information are also given. Individuals present include E. A. Turner, C. J. Biancowicz and F. L. LaQue (Development and Research Dept.)

ROCHESTER ENGINEERING & CENTRIFUGAL CORP.

110 Buffalo Road

Rochester, N. Y.

Booth Nos. 138 and 153

Equipment included in this exhibit are those machines intended especially for the hosiery dyer and silk throwster and include a 50-pound Monel metal rotary hosiery dyeing machine, a 40-inch centrifugal or extractor, a 17-inch centrifugal or extractor and a double unit type Rochester silk impregnator. The following officials and representatives are in attendance: R. C. Caine (General Sales Representative), C. F. Fischer (East), R. S. Shaffer (South), H. C. Rembold (West) and George Blackburn (Britain).

SMITH, DRUM & CO.

Allegheny Ave., below 5th St.

Philadelphia, Pa.

Booth Nos. 23-24-25-26-27-28-29-30

There is here exhibited a line of hosiery dyeing machinery, skein dyeing machines, new motor driven compensating forms and a compensating device for maintaining constant speed on a winding machine. Those in attendance are Harry S. Drum, William C. Dodson, R. D. Howerton and J. E. MacDougall.

JACQUES WOLF & CO.

Passaic, N. J.

Booth No. 350

There is on display samples of various chemical specialties which include a recently perfected oil for one-bath degumming and dyeing operation for silk hosiery. A demonstration by a member of the Wolf technical service is available to any interested company. The booth is in charge of F. G. Henckel (Philadelphia), and during the course of the exhibit will also be attended by J. G. Desmond (Sales Manager), Arnold Pfister (Plant Superintendent), M. F. Costello, G. W. Searell, C. E. Wright and C. J. Rahm.

(Continued on page 250)

OPEN FORUM

Rules under which this department of the REPORTER is conducted are as follows:

1. Anyone who has a technical problem on which he would like advice may submit it to the Reporter and it will be published in the first available issue.

2. Any reader who feels that he has a solution of the problem may forward his reply to us and if we feel that the reply is suitable it will be published in a succeeding issue.

3. For each such reply published the Reporter will pay a minimum of $2.

4. In case there is more than one answer to the same question, the one covering the subject in the most complete and authentic manner will be published, or if two answers are sufficiently different both will be published. If two answers are considered equally good, the one first received will be given priority.

5. The Reporter will assume no responsibility whatsoever for the accuracy of the answers submitted—it is simply offering a vehicle for the public expression of its readers' opinions.

6. Both the questioner and answerer must send in his complete name and address. When requested we will publish only the initials or other identifying insignia.

Answers

2—I understand that the indigisol dyes are being used in wool dyeing. Can you give me any information in regard to the method of application and their fastness properties?—P. V. I.

Answer—The Indigosol dyes are a comparatively new class of dyes used in wool dyeing. They are vat dyes that have been treated chemically to render them soluble. They dye wool directly from an acid bath. The dyed material is aftertreated so that the Indigosol dye is converted back to the vat dye from which it was found. The finished dyeing possesses the same fastness properties that material dyed with the parent vat dye would possess. As a rule this class of dyes possess from good to excellent fastness to light, washing, water, hot pressing, stoving, perspiration, alkali, acid, bleaching, milling, carbonizing, decatizing, salt water and crocking.

There are two methods of dyeing this class of dyes on wool (1) the method used for Indigosol O and Indigosol OR and (2) the method used for the other Indigosol dyes.

Method 1 is as follows: The dye is dissolved by pouring hot water over it and is added to the dyebath. Then add

5% Calcined Glauber Salt
1% Rongalite C, and for pale shades—that is up to 5% dye add
3-8% Acetic Acid, or for medium to full shades.
3-6% Formic Acid.

Enter the material at 105° F. Raise slowly to the boil and boil ½ hour. Then exhaust with

2% Sulfuric Acid.

Boil ¾ hour. Then give a light rinse.

Enter the material into a developing bath made up with

7 parts Sulfuric Acid per 1000 parts developing liquor. Add 2-4 parts Indogosol Soap S.P. per 1000 parts bath to increase the fastness to rubbing. Run cold 10 minutes. Then add the following quantities of sodium nitrite in dilute solution.

.4% for 1% Indigosol O (or less).
.8% for 4% Indigosol O (or less).
1.6% for 10% Indigosol O.
2.7% for 20% Indigosol O.

To Indogosol OR use

.3% for 1% Indigosol OR.
.7% for 4% Indigosol OR.
1.4% for 10% Indigosol OR.
2.4% for 20% Indigosol OR.

Treat Indigosol O dyeings 1 hour at 75° F.

Treat Indigosol OR dyeings ¾ hour at 120° F.

Wash thoroughly. Neutralize with a solution of 2 parts soda ash per 1000 parts water. Then wash and dry.

Method 2 is used in dyeing the other members of this class. In this method dissolve the dye in hot water and add to the dyebath with 5% Ammonium Sulfate. Enter the material at 105° F. Raise to the boil in ½ hour and boil ½ hour. Then exhaust the dyebath with 1-10% Acetic Acid and boil ½-1 hour to exhaust. Rinse and enter into a developing bath of

1-3% Ammonium Sulfocyanide.
.7-3.5% Sodium Bichromate and run 15 minutes at 85° F. Then add
5 parts Sulfuric Acid per 1000 parts developing bath and treat at 185°-195° F. for ½ hour. Wash and neutralize with Soda Ash as in method 1. Then wash and dry.

The amount of Sodium Bichromate varies with the different Indigosol dyes, but in general use at least .7%, for 1-2% dye use 1-2%, and for 2-5% dye use 2-3.%—T. C. D.

New Questions

6.—Can you give me a good working method stating amounts of materials, temperatures, and procedure for weighting rayon (viscose) knit goods? What type of equipment is best suited for the purpose?

Should the goods be bleached before weighting or will the advantage of bleaching be lost by subsequent weighting processing? What precautions are necessary in dyeing? How permanent is the weighting, i.e., to repeated washing of the cloth when made into a garment?

Does the gain in weight of say 15% show much advantage? **R. C. B.**

KNITTING ARTS EXHIBITION

(Continued from page 248)

PROCTOR & SCHWARTZ, INC.

Seventh Avenue at Tabor Road
Philadelphia, Pa.
Booth Nos. 252-253-258-259

This exhibit consists of a working demonstration of the Proctor Automatic boarding, drying and stripping machine for hosiery with a new patented conditioning attachment whereby stockings are given an extra conditioning. Major C. T. Griffith (Manager, Hosiery Dept.) are in charge and will be assisted by Charles S. Tiers, Harry B. Lex and Wm. J. Merrigan, Jr.

W. F. FANCOURT & CO.

516-518 S. Delaware Ave.
Philadelphia, Pa.
Booth No. 185

Textile soaps, oils, specialties, for dyeing degumming and delustering as well as oils for conditioning silk and rayon are shown. Two new products, "Fanco" Aquapel, a new splashproof product and "Fanco" Regenasol D-82, a chemical which prevents and redissolves the formation of lime and most metal soaps. Those in attendance are: W. F. Fancourt, Jr., W. F. Fancourt, 3rd, Charles T. Harvey and Dr. K. A. Pelikan.

SCHOLLER BROS., INC.

Amber and Westmoreland Sts.
Philadelphia, Pa.
Booth Nos. 187-188

At this booth is shown a line of soaps, softeners, sulfonated oils, finishes and specialties for hosiery and knit goods, together with samples of fabrics treated with same. George Pickering, A. J. Ganster, L. M. Boyd, J. F. Noble and F. C. Scholler are in attendance.

ALFRED SUTER

200 Fifth Ave.
New York, N. Y.
Booth No. 54

New testing equipment for silk, rayon, and other fabrics are exhibited as well as the Simon Hosiery Wear Tester. Alfred Suter is in attendance.

W. H. & F. JORDAN, JR., MFG. CO.

3047-49 Amber St.
Philadelphia, Pa.
Booth No. 133

This exhibit consists of textile oils, textile soaps, special softeners, wool lubricants and a new product for softening water. Insecticides and disinfectants are shown. In addition various textile materials finished with the above products are shown. Representatives at the booth are: Canfield Jordan (President), Harold B. Dohner (Treasurer and Chemist), Robert A. Bruce (Philadelphia Rep.) and George C. Harkins (Specialty Rep.)

THE PERMUTIT CO.

330 West 42nd St.
New York, N. Y.
Booth No. 364

Here is exhibited a fully automatic control for zeolite water softeners, single valve control for water softeners and filters, electro-chemical feed, Ranarex CO_2 indicator and recorder, new plate type heat exchanger and fully automatic household water softener. Those in attendance are M. F. Corin, D. J. Hess and W. L. Lowrie.

CLASSIFIED

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

TEXTILE CHEMIST: At present employed by rayon manufacturer but desire change to smaller growing textile, textile chemical, dyeing or consulting firm with prospects for future growth. Five years' experience in all phases rayon manufacture, analytical, research, development and operating. M. S. degree and graduate study in chemical engineering. Southern location preferred. Write Box No. 808, American Dyestuff Reporter, 440 Fourth Avenue, New York, N. Y.

"Wanted to buy, used temperature and humidity control cabinet. Must be in perfect condition. Give price and detailed description. Write Box No. 809, American Dyestuff Reporter, 440 Fourth Avenue, New York, N. Y.

Large manufacturers has an opening for an experienced Dyestuff Salesman to call on Textile Manufacturers. Must be thoroughly familiar with various classes of dyestuffs and particularly vat, naphthol, and fast colors. Write Box No. 810, American Dyestuff Reporter, 440 Fourth Avenue, New York, N. Y.

POSITION WANTED

Colorist-Chemist. Six years' experience in dyestuff and textile fields. Specialist on vat dyes. Experienced in sulfonated oils, textile finishes and sizes. Columbia University trained. Salary secondary to advancement. Must be within commuting distance of New York City. Write Box No. 811, American Dyestuff Reporter, 440 Fourth Avenue, New York, N. Y.